THE PYROLYSIS OF BENZIL AND DESOXYBENZOIN

Ralph Neil Barraclough

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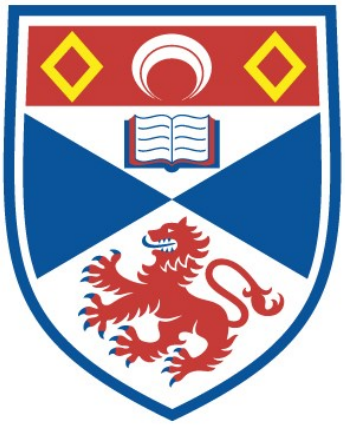

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THE PYROLYSIS OF BENZIL AND DESOXYBENZOIN.

Being a thesis presented by Ralph Neil Barraclough to the University of St. Andrews in application for the degree of Doctor of Philosophy.

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DECLARATION.

I hereby declare that the following thesis is a record of results of experiments carried out by me, that the thesis is my own composition, and that it has not been previously presented for a higher degree.

The experiments were carried out in the Chemistry Research Laboratories of St. Salvator's College, St. Andrews, under the supervision of Dr. C. Horrex.

CERTIFICATE.

I hereby certify that Ralph Neil Berreclough has spent fourteen terms at research work under my supervision, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

UNIVERSITY CAREER.

I matriculated in the University of St. Andrews in October, 1950, and graduated B.Sc. with First Class Honours in Chemistry in June 1954.

The work described in this thesis was carried out during the period from August 1954 to September 1958.

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CONTENTS.

INTRODUCTION

From work which had been carried out recently in the Chemistry Department, St. Andrews, by Pittilo, Alexander and Davidson, it was known that the thermal decomposition of dibenzyl was initiated by a split into benzyl radicals, and that these radicals could also readily recombine to give the parent compound. This preferential fission of the central C-C bond is expected from the stability of the benzyl radicals. This stability can be expressed in theoretical terms by consideration of resonance structures, conjugation of the free electron with the π electrons of the ring, or low heat of formation of the radical.

In this matter of the interaction of a free electron with the aromatic ring the benzoyl radical should resemble in some measure the benzyl radical, and we would, therefore anticipate that benzil should also show a low dissociation energy for the central C-C bond. After this initial decomposition step the thermal decomposition processes would not be expected to be analogous for benzil and dibenzyl since C_6H_5CO radicals have the possibility of decomposing to phenyl radicals and carbon monoxide. A short, qualitative note by Jaquiss and Seware, indicated that when benzil is pyrolysed using the toluene carrier gas technique, this decomposition of the benzoyl radicals does occur extensively.

In view of these facts, it seemed that a study of the thermal

decomposition of benzil might provide interesting material and work was begun using the toluene carrier gas technique with several refinements.

When this work was two years under way, and the rate constants with a temperature coefficient had been obtained, a brief mention in a paper by Clark and Pritchard[2] stated that some quantitative data on the benzil decomposition existed in a Ph.D. thesis of Manchester University by M. Jaquiss (1965).

The data obtained by Jaquiss did not agree with the data detailed in later pages and he had made little attempt to investigate reaction products. As a result, our investigation was continued, and extended to include a shorter study of the pyrolysis of deoxybenzoin $PhCO.CH_2Ph$. This substance was chosen as a link with the pyrolysis of dibenzyl.

Before a description of the experimental work of this research, a brief survey is given of the relevant literature, with respect to the methods of determination of bond dissociation energies, and the properties of radicals which might be expected to be formed in the processes studied.

Bond dissociation energies.

Knowledge of the strength of bonds in organic molecules is of fundamental importance to chemical kinetics since the values are closely related to the reactivities of the compounds. The bond dissociation energy (D) is defined as the endothermicity of the

reaction in which only the bond in question is ruptured, and where the reactants and products are in the gas phase and, for the purposes of rigid definition, at $0^{\circ}K$. Thus it is the value for the reaction at $0^{\circ}K$:

$$R\,X = R + X - D \text{ k cals.}$$

Since the correction to absolute zero is only small (about 1 k cal), values for bond dissociation energies are often based on thermochemical data at room temperature rather than at $0^{\circ}K$. The endothermicity for the above reaction is given by:

$$\Delta H = \Delta Hf_{(g)}(R) + \Delta Hf_{(g)}(X) - \Delta Hf_{(g)}(R\text{-}X) = D(R\text{-}X)$$

From this equation, it can be seen that the problem of determining the bond dissociation energy D(R-X) is directly related to that of finding ΔHf (R) and ΔHf (X). Hence, the use of heats of formation of radicals can lead to bond strength values, or vice versa.

Several methods for the determination of bond dissociation have been evolved, and reviews of them are available.[3,4] As a result, the survey given below is purposely limited in scope and greater detail is given only where this is relevant to the experimental work discussed later.

The methods for measuring the endothermicity of a bond fission can be assembled roughly into three groups:

A Where the energy required is supplied in a controlled or measured way, as in electron impact or spectroscopic experiments.

B Where the energy required for the fission is deduced indirectly

from the variation of equilibrium constant with temperature or from the magnitude of a gaseous equilibrium constant at one temperature and a knowledge of the entropy changes involved.

C Where a rate process has been adequately analysed and use can be made of the relationship that the difference between the energy of activation of the forward and reverse reactions is equal to the change in heat content for the bond fission reaction.

A (1) Electron Impact Methods.

As far as the work outlined in this thesis is concerned, the main interest here has been the deduction of values for the heat of formation of the benzyl radical. The methods have been given in detail by Stevenson,[5] and the general technique is to allow electrons of known energy to produce ionisation and dissociation of the substance under investigation. Under certain conditions the lowest electron energy required to produce a given ion by dissociation and ionisation is equal to the sum of the dissociation energy of the link and the ionisation potential of the fragment.

e.g. suppose the electron bombardment of a molecule AB initiates the process:

$$AB + e = A^+ + B + 2e$$

Then $A(A^+) = D(A-B) + I(A)$ if the ion A^+, and the atom or radical B are in their ground states.

where $A(A^+)$ is the appearance potential of the ion A^+, and I(A) is the ionisation potential of the radical or atom A.

Two general approaches have been made to the deduction of bond dissociation energies from appearance potential measurements:

(a) The indirect method.

The basis of this is the determination of the appearance potential of the same ion in the mass spectra of two different substances; two equations are then set down from which the ionisation potential of the radical A can be eliminated. Schissler and Stevenson[6] applied this method in measuring the appearance potential of the $C_7H_7^+$ ion, which they believed to be the benzyl ion, in the mass spectra of toluene, ethylbenzene and dibenzyl.

The method of calculation was as follows: If it is assumed that the appearance potentials of the $C_7H_7^+$ ion in the mass spectra of toluene and dibenzyl have the significance:

$$C_6H_5.CH_3 = C_7H_7^+ + H + e \quad . \quad . \quad . \quad . \quad (1)$$

$$A_1(C_7H_7^+) = D(PhCH_2\text{-}H) + I\,(PhCH_2\cdot)$$

$$(C_6H_5CH_2)_2 = C_7H_7^+ + PhCH_2 + e \quad . \quad . \quad . \quad (2)$$

$$A_2(C_7H_7^+) = D(C_7H_7\text{-}C_7H_7) + I\,(PhCH_2)$$

Then, by difference:

$$(PhCH_2)_2 + H = PhCH_3 + PhCH_2\cdot \quad . \quad . \quad . \quad (3)$$

and for this reaction, $\Delta H = A_2(C_7H_7^+) - A_1(C_7H_7^+)$

From the heats of formation of toluene and dibenzyl, and D(H-H), ΔH for reaction (4):

$$(PhCH_2)_2 + 2H = 2\,PhCH_2 \quad . \quad . \quad . \quad . \quad (4)$$

can be calculated as -4.66 eV / molecule.

From equations (5) and (4)

$$PhCH_2H = PhCH_2^- + H$$

and $D(PhCH_2\text{-}H) = 4.66 + A_2(C_7H_7^+) - A_1(C_7H_7^+)$

$= \underline{77 \pm 3 \text{ k cal/mole.}}$ [5]

Earlier, Stevenson had pointed out that a dissociation energy deduced in this way could be in error if the two processes did not yield the ion $(C_7H_7^+)$ in the same state, or if either or both processes

$$H + C_7H_7^+ = (C_7H_8^+)$$

$$PhCH_2^- + C_7H_7^+ = (C_7H_7\text{-}C_7H_7^+)$$

require an activation energy. However, Schissler and Stevenson's value for $D(PhCH_2\text{-}H)$ was compared with Szwarc's value (77.5 k cal)[7] from the pyrolysis of toluene, and contrasted with the value of Von Artsdalen et alia (89.9 k cal)[8] from the photobromination of toluene.

(b) The direct method.

It was suggested that appearance potentials of molecule-ions themselves can be reasonably accurately associated with the ionisation potential of the molecule. Thus, the dissociation energy of a benzyl halide $D(PhCH_2\text{-}X)$ might be alternatively calculated as the difference between the appearance potentials of the benzyl ion in the halide mass spectrum and in the benzyl radical mass spectrum.

$$PhCH_2X = (C_7H_7^+) + X \quad . \quad . \quad . \quad . \quad (5)$$

$$A_5(C_7H_7^+) = D(PhCH_2X) + I(C_7H_7^+)$$

$$PhCH_2- = (C_7H_7+) \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

$$A_2(C_7H_7+) = I(C_7H_7+)$$

Such a determination of $D(PhCH_2-X)$ would be greater than or equal to the true value and, if greater, the amount would be by the activation energy of the process

$$X + (C_7H_7+) = (C_7H_7X^+)$$

Lossing, Ingold and Henderson[9] did this for benzyl bromide and iodide, and deduced a value for $I(C_7H_7+)$ in the benzyl radical mass spectrum as 7.75 ± 0.08 eV.

Farmer, Henderson, McDowell and Lossing,[10] in discussing the work of Schissler and Stevenson,[6] pointed out that the ionisation potential of the benzyl radical could be deduced from:

$$I(PhCH_2-) = 2A_1(C_7H_7+) - A_2(C_7H_7+) + 2\,\Delta Hf(PhCH_3) - \Delta Hf(PhCH_2)_2 - 2\,\Delta Hf(H) \quad . \quad . \quad . \qquad (7)$$

$$= \underline{8.51\ eV.}$$

and that this calculation is independent of any bond dissociation energy values in toluene or dibenzyl. They also determined $I(C_7H_7+)$ directly using benzyl radicals from the pyrolysis of benzylamine as 7.81 ± 0.08 eV. The average of the two directly determined values for $I(C_7H_7+)$ then, was 7.76 ± 0.08 eV. If the appearance potential of C_7H_7+ from toluene (11.87±0.1 eV.) is combined with the measured ionisation potential for the benzyl radical (7.76 ± 0.08 eV.) using the equation of the direct method:

$$A(C_7H_7+) - I(C_7H_7) \geq D(C_7H_7-H)$$

and $D(PhCH_2\text{-}H) \simeq 95$ k cal.

The discrepancy between this value and 77 ± 3 k cals. is equal to the discrepancy between the derived and measured ionisation potentials for benzyl. Therefore, either $A(C_7H_7^+)$ from toluene is too high or the measured ionisation potential of the benzyl radical is too low by ~ 0.80 eV.

From the close similarity of the mass spectra of toluene and cycloheptatriene, and from investigation of the mass spectrum of toluene-$-C^{13}$, Meyerson and Rylander[11] suggested that the $C_7H_7^+$ ion produced in all these mass spectra is the tropyllium, and not the benzyl ion. They calculated the apparent heat of formation of the $(C_7H_7^+)$ ion and found it was the same for ions from toluene, ethylbenzene, propylbenzene, dibenzyl and cycloheptatriene. They suggested that the reverse reaction

$$C_7H_7^+ + H = C_7H_8^+$$

may require an activation energy of at least 0.7 eV., and that the appearance potential of the $(C_7H_7^+)$ ion from toluene, which Schissler and Stevenson determined, was for the tropyllium ion, and this might be higher than that for the benzyl radical by about 0.7 eV. Thus $D(PhCH_2\text{-}H)$ determined by the direct method might be in error by this amount.

In the determination of $D(PhCH_2\text{-}H)$ by the indirect method, taking the difference of the appearance potentials of the same ion from two different, but related molecules would eliminate excess energy terms

if these were similar, and would give the true D. Even if the excess energy terms were not the same this method might give a better value for $D(PhCH_2-H)$ than the direct method, depending on the relative size of the excess energy terms. i.e. 77.0 might be nearer the truth than 95.0.

(2) Spectroscopic methods.

These are not generally applicable to polyatomic molecules and so are not of immediate interest. They may be summarised briefly in two groups:

(a) Methods where absorption bands corresponding to vibrational energy changes for low values of the vibrational quantum number are observed - the energy levels are fitted by a formula and

(i) the plot of the energy of each level against its vibrational quantum number is extrapolated to the limiting quantum number.

(ii) the energy change between adjacent vibrational levels is plotted against the vibrational quantum number for the lower vibrational energy changes, and the area under the curve measured.

Either procedure, when applied to vibrational transitions associated with an electronic transition gives the energy for the dissociation.

$$X\,Y = X^{*} + Y$$

excited

Where vibrational bands are obtainable for the ground state, the method may be applied in either way to obtain the dissociation energy

for

$$XY = X + Y$$

where neither X nor Y is excited.

(b) Where a continuum is observed in the spectrum of a molecule XY the frequency of the onset of the continuum gives $h\nu$ for the dissociation

$$XY = X^{*} + Y$$

excited

To determine D(XY) when either of the atoms X,Y is excited, the excitation energy must be known.

B Equilibrium methods.

If the equilibrium constant for a gaseous reaction

e.g. $R_1R_2 \rightleftharpoons R_1 + R_2$ is known over a range of temperatures, the heat of dissociation may be deduced using the integrated Van't Hoff isochore $\ln Kp = \frac{-\Delta H}{RT} + \text{const.}$ If the equilibrium constant is known at one temperature, then the change in free energy can be calculated from $\Delta F^{\circ} = -RT \ln Kp$.

Since $\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, assessment of the entropy change will lead to the energy required for the fission, ΔH.

Benson and Buss[12] measured the equilibrium constant for the reaction

$$PhCH_3\ (g) + Br_2\ (g) \rightleftharpoons PhCH_2Br\ (g) + HBr\ (g)$$

at 130°C, approaching the equilibrium from both sides; and calculated $\Delta F^{\circ}_{(425^{\circ}K)}$ using the expression $\Delta F^{\circ} = -RT \ln Kp$. They calculated $\Delta S_{(425^{\circ}K)}$ for the reaction, using an entropy value for benzyl

bromide obtained from spectroscopic data, and found $\Delta H_{(298^\circ K)}$ for the reaction using the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$. Their value of -8.0 ± 0.90 k cal. for $\Delta H_{(298^\circ K)}$ was about 6 k cal. higher than the value derived from the bond energies $D(PhCH_2-H)$ and $D(PhCH_2Br)$ assigned from kinetic studies by Szwarc[7], and hydrolysis studies by Gellner and Skinner[13].

After discussing the various possibilities, Benson and Buss suggested that the value $D(PhCH_2-H) = 77.5$ of Szwarc is probably low. In an effort to solve the problem of the bond dissociation energy of toluene they reviewed the available experimental data for the heat of formation of the benzyl radical. These values ranged between 38 and 45 k cals. and are summarised and discussed later in the thesis along with the results of the present work.

C The Kinetic Method.

This usually involves:

(a) the establishment of a mechanism for a process which involves all the atoms and radicals, and which permits the deduction of the energy changes involved.

(b) the calculation from this mechanism of the activation energy of an elementary reaction of the type

$$R\,I = R\cdot + I\cdot$$

(c) the assumption that the activation energy of this reaction is equal to the dissociation energy of the bond being broken. This is the same as assuming that the activation energy for the reverse reaction

TABLE 1

Iodide	Q* (k cal)
methyl	53 - 55
ethyl	52.2
n-propyl	50.0
n-butyl	49.0
isopropyl	46.1
tert-butyl	45.1
allyl	59.0
vinyl	55.0
benzyl	45.7
phenyl	54.0
acetyl	(50.7)
benzoyl	43.9
acetonyl	45.0
cyclohexyl	49.2
phenylethyl	50.0
dichloromethyl	42.4
dibromomethyl	41.4
diiodomethyl	(37)
chloroethyl	45.9

is zero, which is believed to be a reasonable assumption in many cases.

It must be emphasised that unless all the R- and X- radicals are accounted for, accurate deductions about the strength of the R-X bond cannot be made by this method. Much of the early bond dissociation energy data are not reliable as sufficient precautions to suppress side reactions were not taken, and a detailed enough examination of the products was not made, so that the mechanism was uncertain.

e.g. (1) Rice et alia[14] refined an earlier technique of Paneth and Hofedits[15] and pyrolysed organic compounds in the presence of a metallic mirror and under conditions of low pressure and short contact time, but the time lag between the furnace and the mirror was probably too great and side reactions occurred, producing complication and error.

(2) Polanyi and co-workers[16] carried out the pyrolyses of several iodides under conditions of slow pressure and fast flow. The decompositions were carried out at about 400-500°C, to only a few per cent conversion, and the progress of the reaction was followed by the amount of free iodine formed. The results of these experiments are shown in table 1 opposite. For some of the iodides, variation of the iodide partial pressure showed the decomposition to be roughly first order. Many of the decompositions, however, are not first order and some doubt is thrown on the value of the bond dissociation energy values quoted. In a number of cases they calculated an energy of

activation from the value of the velocity constants at one temperature by assuming that $k = 10^{13} e^{-E/RT}$ was applicable.

(3) Experiments in static systems[17] showed that the decomposition of iodides was complicated by the reaction

$$R\text{-} + I\text{-} = RI$$

so these systems cannot be used to determine the bond dissociation energy of the initial split

$$RI = R\text{-} + I\text{-}$$

For the photobromination of toluene, however, Von Artsdalen et alia[18] were able to elucidate the mechanism fully and hence determine the bond dissociation energy $D(PhCH_2\text{-}H)$. The steps involved were:

$Br_2 + h$	$= 2\,Br$	(1)
$Br_2 + M$	$= 2\,Br + M$	(1a)
$Br + RH$	$= R\text{-} + HBr$	(2) where $R = PhCH_2\text{-}$
$R\text{-} + Br_2$	$= RBr + Br\text{-}$	(3)
$R + HBr$	$= RH + Br$	(4)
$Br + Br + M$	$= Br_2 + M$	(5)

The average activation energy was determined, and assigned to reaction (2). i.e. $E_2 = 7.2$ k cal/mole. Also, $E_4 - E_5$ was determined as 5.0 k cal/mole

Since reaction (3) is an exothermic radical reaction, it was assumed that it proceeds with zero activation energy.

$$\therefore E_4 = 5.0 \text{ k cal/mole.}$$

This however, is a minimum, and will be higher if E_3 has a small

positive value.

Since the activation energy for step (4) is equal to the activation energy for the reverse of reaction (2), the endothermicity of reaction (2), $\Delta H_2 = E_3 - E_4 = 2.2$ k cal/mole at the experimental temperature of 381°K.

Hence $Br + RH = R + HBr$, $\Delta H_{381} = 2.2$ k cal/mole

$HBr = H + Br$, $\Delta H_{381} = 87.7$ k cal/mole

$RH = R + H$, $\Delta H_{381} = 89.9$ k cal/mole.

The heat of formation of the benzyl radical was computed from the expression $\Delta Hf\ (R) = \Delta Hf\ (RH) - \Delta Hf\ (H) + D(R-H)$ and the values obtained are shown below:

TABLE 2

Temperature (°K)	$\Delta Hf\ (PhCH_2\cdot)$	$D(PhCH_2-H)$
0	55.9 ± 1.4	88.1 ± 1.4
298	49.4 ± 1.4	89.5 ± 1.4
381	48.4 ± 1.4	89.9 ± 1.4

[19]

Benson and Buss suggest that the reaction

$$Br + Br + M = Br_2 + M$$

may not take place so quickly as was assumed, and that the rate law may not be so simple as was assumed. The application of this direct method to other hydrocarbons has not given quite the same amount of information.[20]

Toluene carrier technique.[21]

Under certain conditions, toluene was found to act as a radical trap, and this property is used in the toluene carrier technique. The substance of unknown bond strength is pyrolysed in the presence of excess toluene, and the radicals from the initial split

$$R_1R_2 = R_1\cdot + R_2\cdot$$

react with the toluene usually by extraction of hydrogen.

$$R_1\cdot + PhCH_3 = R_1H + PhCH_2\cdot$$

$$R_2\cdot + PhCH_3 = R_2H + PhCH_2\cdot$$

The benzyl radical is unreactive and eventually dimerises.

$$2\ PhCH_2\cdot = (PhCH_2)_2$$

Thus the radicals R_1, R_2 are prevented from complicating the initial reaction e.g. by back reaction or chain initiation and if there is some method of estimating the extent of decomposition of R_1R_2, it may be possible to measure the rate of decomposition over a range of temperatures and deduce $D(R_1\text{-}R_2)$. The toluene is usually present in large excess as a carrier gas and the conditions of the experiment are fast flow and low percentage decomposition.

An extensive series of decompositions were carried out by the method[22] and a good illustration of the simplification effected by its use is the thermal decomposition of ethylbenzene. Without toluene, the decomposition is complex:

$$PhC_2H_5 = PhCH_2\cdot + CH_3\cdot$$

$$CH_3\cdot + PhC_2H_5 = CH_4 + PhC_2H_4$$

$$PhC_2H_4 = PhCH = CH_2 + H\text{-}$$

$$H\text{-} + PhC_2H_5 = PhC_2H_4 + H_2 \quad \text{, etc.}$$

With excess toluene present the reaction is greatly simplified since the methyl radical from the initial split reacts readily with the toluene

$$PhC_2H_5 = PhCH_2\text{-} + CH_3\text{-}$$

$$CH_3\text{-} + PhCH_3 = CH_4 + PhCH_2\text{-}$$

$$2PhCH_2\text{-} = (PhCH_2)_2$$

The rate of production of methane is thus a measure of the rate of the initial split, and by measurements of the methane production, $D(PhCH_2\text{-} CH_3)$ was deduced as 85 k cal.

An early application of the method was to the decomposition of toluene itself.[7,23] Szwarc pyrolysed toluene by a fast flow technique at very small conversion. He found the gaseous products to be a mixture of hydrogen and methane in the ratio 1.6 to 1, and that this ratio did not vary appreciably with temperature. On the basis of only a few experiments he assumed the mechanism to be:

$$PhCH_3 = PhCH_2\text{-} + H \qquad (1)$$

$$H + PhCH_3 = PhCH_2\text{-} + H_2 \qquad (2)$$

$$H + PhCH_3 = PhH + CH_3 \qquad (3)$$

$$CH_3\text{-} + PhCH_3 = PhCH_2\text{-} + CH_4 \qquad (4)$$

$$2PhCH_2\text{-} = (PhCH_2)_2 \qquad (5)$$

From measurements of the amount of gaseous product under various conditions, he deduced that the reaction was homogeneous and of the

first order, and that the experimental activation energy, assigned to reaction (i), was 77.5 ± 1.5 k cal/mole.

More recent work by Blades, Blades and Steacie,[24] although confirming some of the points put forward by Szwarc, suggests that hydrogen forms 69% of the gaseous products, and that the "dibenzyl", characterised by Szwarc by relatively crude methods was, in fact, a mixture of isomeric dimethyldiphenyls. An apparent activation energy of 90 k cal. was found, but the "first order constants" varied markedly with contact time and with the condition and extent of the surface.

More recent determinations of the heat of formation of the benzyl radical[12] suggest that 77.5 k cal. is a rather low figure for $D(PhCH_2-H)$ and Szwarc's determination is perhaps an example of unjustified estimation of the activation energy for a step in a total mechanism, before the mechanism had been fully established.

Limitations to the toluene carrier technique can be briefly summarised:

(a) As applied by early workers, the experimental method was unsatisfactory for kinetic work of any accuracy. Toluene vapour was passed over the reactant in a sealed U-tube and carried forward entrained reactant vapour through the furnace. Solution of the toluene in the reactant in some cases, made the concentration of reactant in the furnace indeterminate and in the apparatus used by Szwarc et alia, it was not possible to vary independently the concentrations of toluene

and reactant, and the contact time. The method can be adapted to overcome these faults however, as is later described.

(b) The method cannot be used to determine bond dissociation energies greater than that for the C-H bond in toluene. Most favourably the dissociation energy of the bond to be broken should be at least 10 k cals. less than $D(PhCH_2\text{-}H)$.

(c) The atom or radical R produced in the initial dissociation should react easily with toluene to give the stable molecule RH. The technique is also possible when the radical initially formed decomposes rapidly to give another reactive radical.

e.g. $RCO\text{-} = R\text{-} + CO$

then $R\text{-} + PhCH_3 = RH + PhCH_2\text{-}$.

(d) For compounds with very low bond dissociation energy the temperature for decomposition is so low that the reaction

$$PhCH_3 + R = RH + PhCH_2\text{-}$$

is slow, and the radicals may dimerise etc., instead of reacting with the toluene.

e.g. the decomposition of ditertbutyl peroxide at 200°C produces methyl radicals which dimerise to ethane rather than react with the toluene.

For the decomposition of benzyl iodide, the reaction between iodine atoms and toluene is very slow

$$I + PhCH_3 = HI + PhCH_2\text{-}$$

and recombination occurs $I + PhCH_2\text{-} = PhCH_2I$.

In this case there may also be reaction between iodine molecules and benzyl radicals.[25]

An additional possible complication to simple kinetics is the interaction or decomposition of any of the entities present at the reaction vessel wall. In many cases the effect of the wall is difficult to assess, and it may prove an obstacle to reliable measurements.

Phenyl, benzoyl and benzyl radicals.

The preliminary work of Jaquiss and Szwarc[1] suggests that these three radicals are involved in the pyrolysis of benzil by the toluene carrier technique, so it would be interesting to survey briefly other reactions in which they are present.

In 1952, Zartman and Atkins[26] reported quantitative production of diphenyl from tetraphenyl lead in the presence of nickel and hydrogen at 200°C. In 1955, Dull and Simons[27] performed an experiment revealing the mechanism of the diphenyl formation, and proving the existence of phenyl radicals. Tetraphenyl lead was decomposed thermally (215-320°C) in the presence of mercury vapour, and diphenyl and mercury diphenyl were found amongst the products. Horn and Polanyi[28] produced the phenyl radical by the diffusion flame method, and detected its presence by reaction with iodine.

Some evidence for the radical was found by the photolysis of tetraphenyl lead in benzene solution.

[30]

Paneth and Lautsch repeated Dull and Simon's experiments with tetraphenyl lead and could find no evidence for the reaction of phenyl radicals with either tellurium or lead. However, the temperature used (red heat) was much higher than that of Dull and Simons, and deposition of carbon indicated extensive decomposition.

Paneth and Lautsch also repeated Horn and Polanyi's experiments and could still find no evidence for phenyl reaction with tellurium. They concluded that either the phenyl radical did not react with tellurium, or was much less stable than ethyl or methyl.

In an attempt to clear up the situation Glasebrook and Pearson[31] studied the effect of the photolysis of aromatic ketones (at 150°C) in the presence of tellurium mirrors. The presence of free methyl and phenyl radicals in the photolysis of acetophenone was detected by their reaction with tellurium. Photolysis in the absence of tellurium gave products which showed the melting points of diphenyl, benzil, and possibly dibenzyl ethane. The occurrence of benzil suggests the intermediate formation of the benzoyl radical (C_6H_5CO-), which can dissociate into a phenyl radical and carbon monoxide.

Schüler and Reinbeck[32] decomposed a number of benzene derivatives into both excited and unexcited radicals by electron impact. Both identical (i.e. radical) and characteristic emission spectra were observed. The phenyl radical was found for benzene and for a number of monosubstituted benzenes, including toluene. The benzoyl radical was detected for acetophenone and benzophenone, and there was some

evidence for the existence of the radical for benzaldehyde.

The benzyl radical was first produced in 1935 by Panth and Lautsch[30] by the thermal decomposition of tetrabenzyl tin, dibenzyl ketone, and by the reaction of benzyl chloride with sodium vapour. The radical was detected by reaction with mirrors of selenium, tellurium and mercury. The radical has been found in the thermal decomposition of toluene in the presence of mercury vapour[33] and by the detection of dibenzyl.[7] The benzyl radical has been produced in the decomposition of some substituted toluenes[34] and by the production of free radicals in the presence of toluene (viz: by the "toluene carrier" technique).

More recently, mass spectrometric observation of the products of thermal decomposition of some aromatic compounds by Loesing and Ingold[35] has given direct evidence for the presence of phenyl, benzoyl and benzyl (or tolyl) radicals. The aromatic compounds were decomposed in a furnace immediately above the mass spectrometer leak, so that some radicals could enter the instrument without suffering collision. Some of the compounds decomposed were toluene, benzaldehyde, diphenyl, anisole and benzyl ether. With the technique used, it was not possible to deal with compounds as involatile as benzophenone or benzil. The furnace temperature was varied and the decay of radical peaks with increasing temperature plotted.

Since the temperatures to secure sufficient decomposition for analysis were rather high ($\sim 1000^{\circ}C$) the number of possible alternative

radical reactions (e.g. decomposition or hydrogen extraction) was large, and it was not possible to assign the measurements of radical peak decay to any one reaction. The general indication, however, was that phenyl and benzyl radicals could be obtained abundantly below 1150°C, whereas the benzoyl radical appears to be less stable, and could not be obtained in large amounts from any of the compounds studied.

In solution, there is good evidence for the phenyl radical as an intermediate in the reactions of benzene diazonium chloride[36] and in the action of copper bronze on phenyl iodide.[37] Kharasch et alia[38] suggest a mechanism for the reaction of azobenzene and benzaldehyde in the presence of tert. butyl peroxide, involving the benzoyl radical as a chain intermediate.

Decompositions involving the benzoyl radical.

At lower temperatures than those of the experiments of Lossing and Ingold,[35] the benzoyl radical appears to be more stable. Since the stability of this radical is so dependent on the temperature, it may be convenient to divide the reactions arbitrarily into those carried out above, or below 300°C:

(a) "High temperature" reactions. (>300°C)

In 1948 Butler and Polanyi[39] pyrolysed several organic iodides in a flow system and followed the extent of the reaction by estimating the free iodine produced. Benzoyl iodide was studied over the temperature range 300 - 450°C. Since no precautions were taken to

prevent the products from interfering (apart from using a low pressure of reactant) the molecularity of the reaction was rather uncertain, but it was noted e.g. that the rate of decomposition for benzoyl iodide was much greater than for ethyl iodide. Unfortunately, no measurements of the carbon monoxide were made.

In 1962, Ladacki, Leigh and Szwarc published work[40] on the thermal decomposition of benzoyl bromide by the toluene carrier technique. This method should ensure that the products did not interfere with the simple initial split. All the products except benzene (from the reaction of phenyl with toluene) were analysed for, and the mechanism was suggested to be an initial split to benzoyl and bromine

$$PhCOBr = PhCO\cdot + Br$$

followed by the rapid decomposition of the benzoyl radical

$$PhCO\cdot = Ph\cdot + CO$$

Dibenzyl was formed by dimerisation of the benzyl radicals which were by-products of the hydrogen-extraction reaction of phenyl on the toluene:

$$Ph\cdot + PhCH_3 = PhH + PhCH_2\cdot$$

There was no quoted evidence for any other reaction of the benzoyl radical. The reaction was studied from 541 to 675°C and the activation energy of 57 k cals/mole attributed to the bond dissociation energy for the initial split.

The heat of formation of the benzoyl radical could hence be calculated from the expression

$$D\ (PhCO - Br) = \Delta Hf(PhCO) + \Delta Hf(Br) - \Delta Hf(PhCOBr)$$

and $\Delta Hf\ (PhCO) = 15.6 \pm 1$ k cal/mole.

Experiments with a packed vessel verified that the decomposition was homogeneous and in the gas phase.

In 1954, Szwarc and Taylor[41] pyrolysed benzoyl chloride by a similar technique and analysed for all the products as had been done for benzoyl bromide. The decomposition was studied from 600 to 807°C and the mechanism again found to be a unimolecular, first order split

$$PhCOCl = PhCO- + Cl$$

followed by a rapid decomposition of the benzoyl radical

$$Ph\ CO- = Ph- + CO$$

The decomposition was slightly heterogeneous.

The activation energy of 75.6 k cal/mole, obtained from an Arrhenius plot, was assigned to the bond dissociation energy for the initial split. Whereas the frequency factor for the benzoyl bromide decomposition (5×10^{15}) was within the "normal" range, the factor for the benzoyl chloride decomposition (2.5×10^{15}) was "high". No explanation has been offered for this.

From the bond strength D(PhCO-Br) = 75.6, the heat of formation of the benzoyl radical was deduced.

$$\Delta Hf\ (PhCO-) = D(PhCO-Cl) - \Delta Hf(Cl) + \Delta Hf(PhCOCl)$$

$$= 15.7 \pm 1k \text{ cal/mole.}$$

This value is in very good agreement with that from the benzoyl bromide results.

The kinetic data and the stoichiometry of the two latter pyrolyses did not permit distinction between the two possibilities of initial reaction, namely:

(a) $PhCOCl = PhCO\cdot + Cl$ followed by the rapid reaction

$PhCO\cdot = Ph\cdot + CO$

and (b) $PhCOCl = Ph\cdot + COCl$ followed by the rapid reaction

$COCl = Cl + CO$

The distinction was made, however, by comparison of the data obtained. Assuming that mechanism (a) is the true one, the calculated heats of formation of the benzoyl radical from the results of the two pyrolyses are in good agreement.

However, assuming (b) as the correct mechanism, Szwarc and Taylor calculate that $D(COCl) - D(CCl_3) = -0.1$ k cal/mole, which is not reasonable. It is, therefore, inferred that (a) is the correct initial split.

Also, from photosynthesis data on phosgene by Burns and Dainton[42] the dissociation energy of the COCl molecule can be calculated as 6.3 k cal/mole. Hence a value of 96 k cal/mole can be calculated for the Ph - COCl bond dissociation energy. This value is far too high to account for Szwarc and Taylor's experimental data, which gives further evidence in favour of the initial reaction:

$$Ph\ CO\ Cl = PhCO\cdot + Cl$$

Jaquiss and Szwarc, in their briefly reported work on benzil assumed a unimolecular split to two benzoyl radicals

$$PhCOOOPh \rightarrow 2\ PhCO\cdot$$

followed by a rapid decomposition of these radicals:

$$PhCO\cdot \rightarrow Ph\cdot + CO$$

They found dibenzyl as a product, which suggested that the phenyl radicals extract hydrogen from the toluene side-chain, but no attempt was made to estimate or even look for the benzene formed. Since the purity of the dibenzyl was checked only by a rough melting point, the constitution was not fully confirmed. No search was reported for products of the reaction of the benzoyl radical other than its decomposition to phenyl and carbon monoxide.

(b) Low temperature reactions. ($< 300^{\circ}C$)

In 1923, Porter Rampsberger and Steel[43] photolysed benzil vapour at $200^{\circ}C$ and obtained equimolar amounts of benzophenone and carbon monoxide. The reaction did not occur at this temperature without irradiation, and may have been a molecular rearrangement rather than propagated by a free radical mechanism.

In experiments by Glazebrook and Pearson[31] on the photolysis of acetophenone at $< 150^{\circ}C$, benzil was detected as a product. The indication seems to be that the benzoyl radical lives long enough at these temperatures to dimerise.

C.E.H. Bawn,[44] notes the observation of Hurcamps[44] that benzil is formed as a product when benzoyl chloride and sodium vapour are allowed to react at $240^{\circ}C$ by the sodium flame technique.

From these two groups of observations we can deduce that the two modes of reaction available to benzoyl radicals in the vapour phase appear to be dimerisation, or decomposition to phenyl and carbon monoxide, with an increasing tendency to decomposition at high temperatures.

Stability of Radicals.

C.E.H. Bawn, in a discussion on the stability of some aliphatic radicals,[45] notes that the methyl radical is stable up to 1100°C. This is supported by the work of Loesing and Ingold.[35]

Steacie[46] points out that the transitory nature of radicals is not necessarily due to their lack of intrinsic stability, but rather to their high reactivity, which results in their rapid disappearance by reaction with themselves or with other substances which may be present.

According to Bawn,[45] acetyl and other radicals of this type will decompose preferentially according to the scheme:

$$RCO\text{-} \rightarrow R\text{-} + CO$$

since about 77 k cal. is gained by rearrangement of the CO group to carbon monoxide. From calculations of the energy surfaces of the two states of the system, Bawn estimated the activation energy for this decomposition of acetyl as 16 k cal.

Spence and Wild[47] performed experiments on the photolysis of acetone and measured the diacetyl produced, and Feldmann, Blacet and Burton[48] performed experiments by a mirror technique to compare the reactivity

TABLE 5

Halide	D (k cal/mole)	Source of data.
PhCO-Cl	78.6	Szwarc & Taylor JCP 22 20 (1954)
$PhCH_2$-Cl	68.0	" " "
PhCO-Br	57.0	Ladacki, Leigh & Szwarc. PRS A214 375 (1952)
$PhCH_2$-Br	50.5	Szwarc & Ghosh JCP 17 744 (1949) Szwarc & Sehon 18 1142 (1950) Gellner & Skinner JCS 1949 1145
Ph-Br	70.9	Szwarc & Williams JCP 20 1171 (1952)
$PhCH_2$-I	45.2 ± 2	Calc[d]. thermochemically Ubbelohde et alia JCS 1955(1) 115.
Ph-I	60.9 ± 2	" "

of acetyl and methyl radicals. Unfortunately, similar experiments have not been carried out with benzoyl and phenyl radicals.

Roberts and Skinner[49] discussed theoretical aspects for the resonance stabilisation of the acetyl radical, but since this involves hyperconjugation, the mechanism of stabilisation of the benzoyl radical must be different, and the thermal behaviour of the two radicals cannot be closely compared.

In 1952 Szwarc and Williams[50] pyrolysed bromobenzene and deduced the heat of formation of the phenyl radical as

$$\Delta Hf\ (Ph\text{-}) = +\ 69.6 \text{ k.cals.}$$

From this and the heat of formation of the benzyl radical a value for the radical bond dissociation energy for the process

$PhCO\text{-} = Ph\text{-} + CO$ can be calculated.

$$D\ (Ph\text{-}CO\text{-}) = \Delta Hf\ (Ph) - \Delta Hf\ (PhCO) + \Delta Hf(CO)$$

$$= 69.6 - 15.6 - 26.42$$

$$= 27.6 \text{ k cal/mole.}$$

If this estimate is correct, for experiments at higher temperature than 300°C, the benzoyl radical would be quite short-lived.

Some data on the bond dissociation energies of the halides of the phenyl, benzoyl and benzyl radicals has been determined, and is summarised in table 3 opposite. These data were all determined below 870°C, and suggest that the benzoyl radical is more resonance stabilised than the phenyl radical, but less than the benzyl radical. The phenyl radical might, therefore, be expected to be comparatively

reactive. The experiments of Loading and Ingold suggest that at about 1000°C, the benzoyl radical is less stable than the phenyl radical.

After this preliminary literature survey, an account of the present research follows.

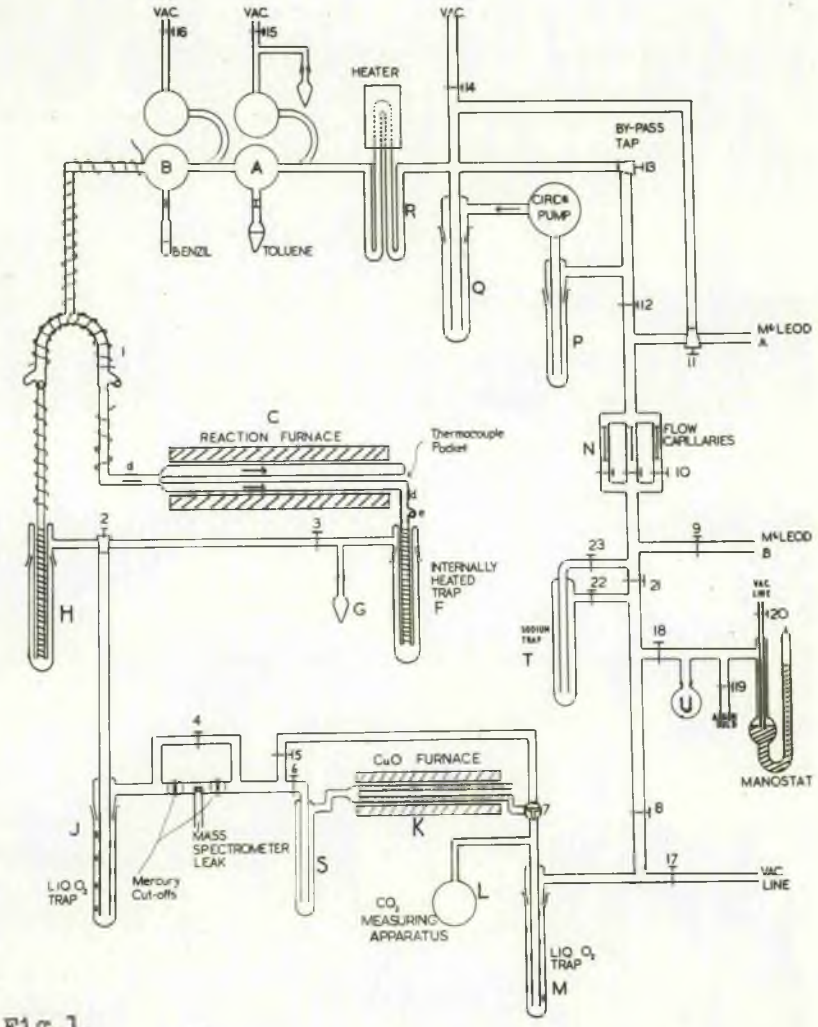

VAC.
16
VAC.
15
HEATER
V/C
14
BY-PASS
TAP
13
B
A
BENZIL
TOLUENE
R
CIRC.
PUMP
Q
P
12
McLEOD
A
11
1
C
REACTION FURNACE
Thermocouple
Pocket
d
N
FLOW
CAPILLARIES
10
2
3
9
McLEOD
B
23
22
21
INTERNALLY
HEATED
TRAP
F
H
G
VAC
LINE
20
SODIUM
TRAP
T
18
U
19
MANOSTAT
4
5
6
CuO FURNACE
7
8
J
MASS
SPECTROMETER
LEAK
S
K
LIQ O2
TRAP
Mercury
Cut-offs
17
VAC.
LINE
CO2
MEASURING
APPARATUS
L
LIQ O2
TRAP
M

Fig.1.

APPARATUS AND EXPERIMENTAL TECHNIQUE.

The experiments performed could be divided into two groups:-

(a) The flow experiments were carried out in a system with continuous circulation of the carrier gas. To permit the analysis of carbon monoxide (at mass 28) on the mass spectrometer, argon was used as the carrier gas at pressures of about 2.0 - 2.5 mm.

(b) Static experiments were performed in separate bulbs, and the products analysed as described in the following section.

A general description of the apparatus and technique common to most of the flow experiments with benzil (deoxybenzoin) and toluene is given below and modifications for particular experiments are described in the later section in which descriptions of these experiments occur.

A diagram of the flow system for experiments using toluene as a radical catcher appears facing P. 30.

Unless stated otherwise, the apparatus and technique for benzil were used also for deoxybenzoin.

The Vacuum Line.

The apparatus was evacuated by a mercury diffusion pump and two-stage rotary oil pump, and the pressure could normally be reduced to less than 10^{-3} mm. mercury, as read on a McLeod gauge.

Graphs to find the optimum Circulation Pump Conditions.

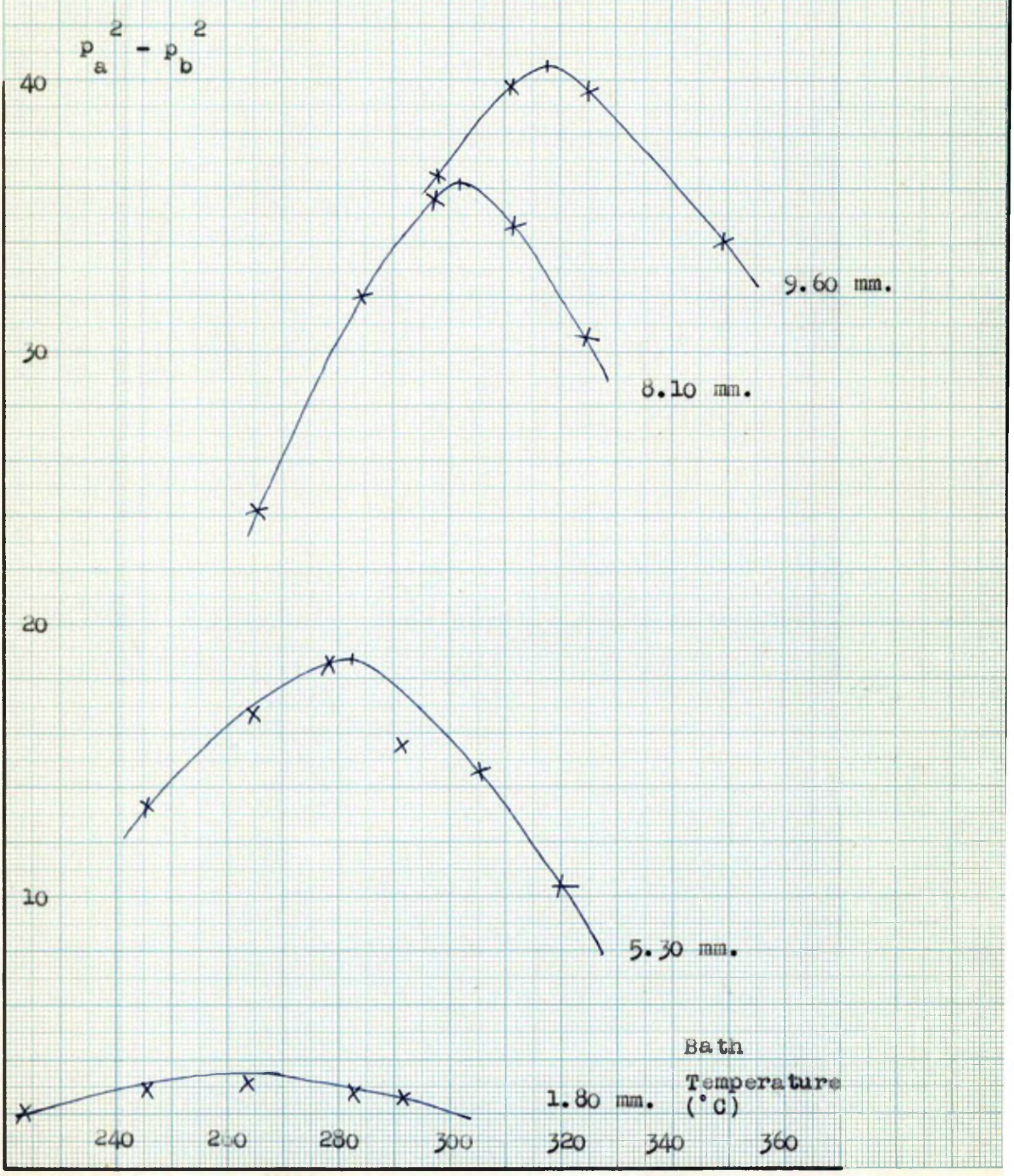


Fig. 2.

The centre curve shows the optimum pump bath temperature for maximum flow rate. The outer curves show the temperature for a 10% drop in flow rate.

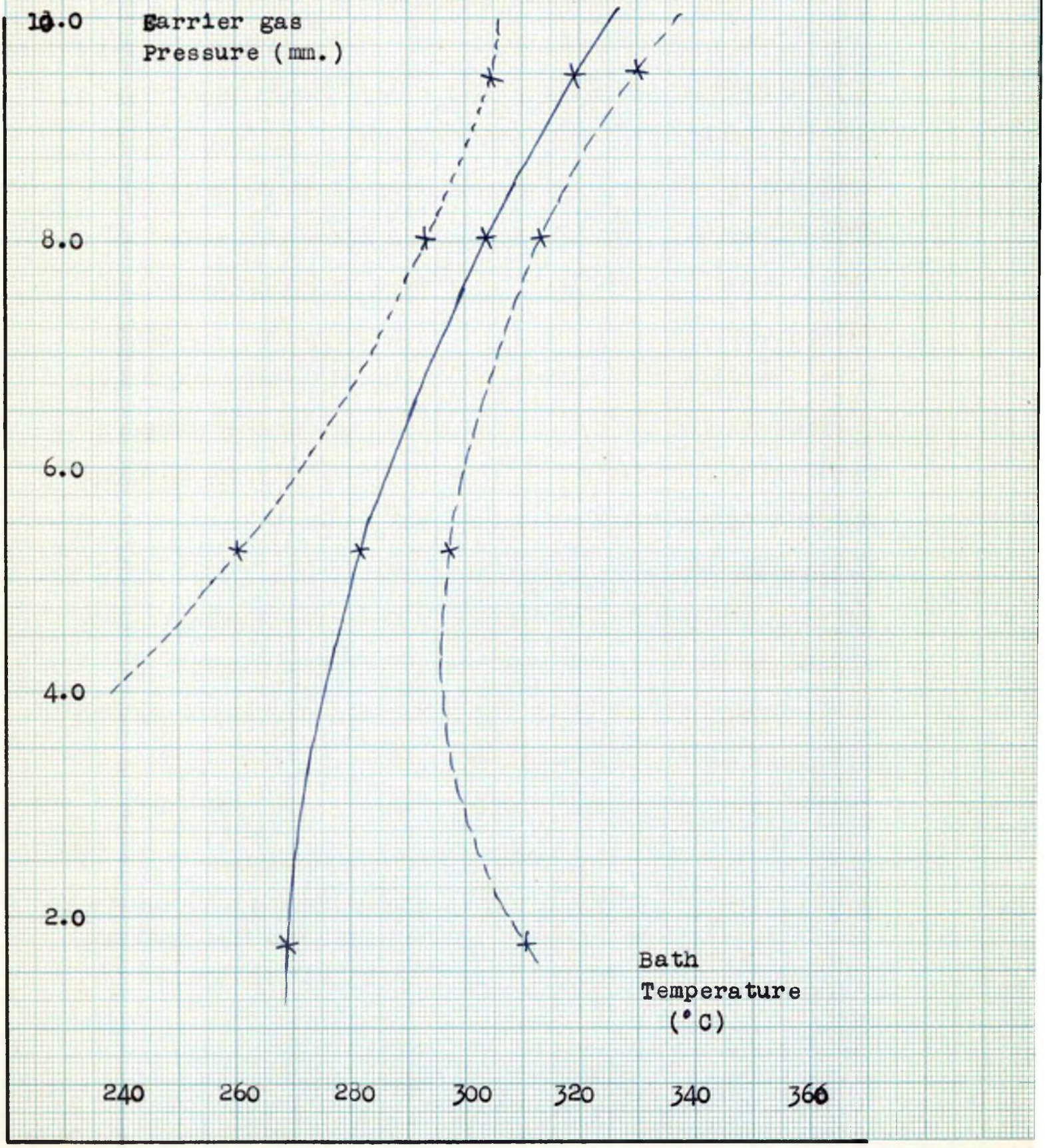


Fig. 3.

The Circulation Pump.

This was a mercury pump with triple jets, heated by a lead - tin solder bath which could be maintained at a fixed temperature ($\pm$ 0.5°C) by a Sunvic energy regulator. It has been demonstrated [51] that the optimum performance of such a pump depends on both the bath temperature and on the carrier pressure. The pump was calibrated by plotting the flow rate against bath temperature, at different carrier gas pressure. Hence a curve was constructed showing the optimum bath temperature for a particular carrier gas pressure, and was used in the subsequent experiments. (Graphs facing. Figs 2,3). During an experiment, cardice cooled traps on either side of the pump and a demister consisting of alternate heated and cooled sections after the pump, prevented the diffusion of mercury vapour into the apparatus.

Flow capillaries.

To measure the rate of carrier gas flow, the pressures across a calibrated capillary were measured by two McLeod gauges. A modification of Poiseuilles law by Meyer gives the rate of gas flow in terms of these pressures and the dimensions of the capillary.

The number of moles gas flowing / sec. $n = \frac{\pi r^4 (Pb^2 - Pa^2)}{16\, l\, R\, T\, \eta}$

where r (cm) = radius of capillary
Pb (dynes/cm^2) = pressure before flow capillary
Pa " = pressure after flow capillary
η (poise) = viscosity of carrier gas
l (cm) = length of capillary
R = gas constant
T (°K) = temperature

CAPILLARY CALIBRATION APPARATUS

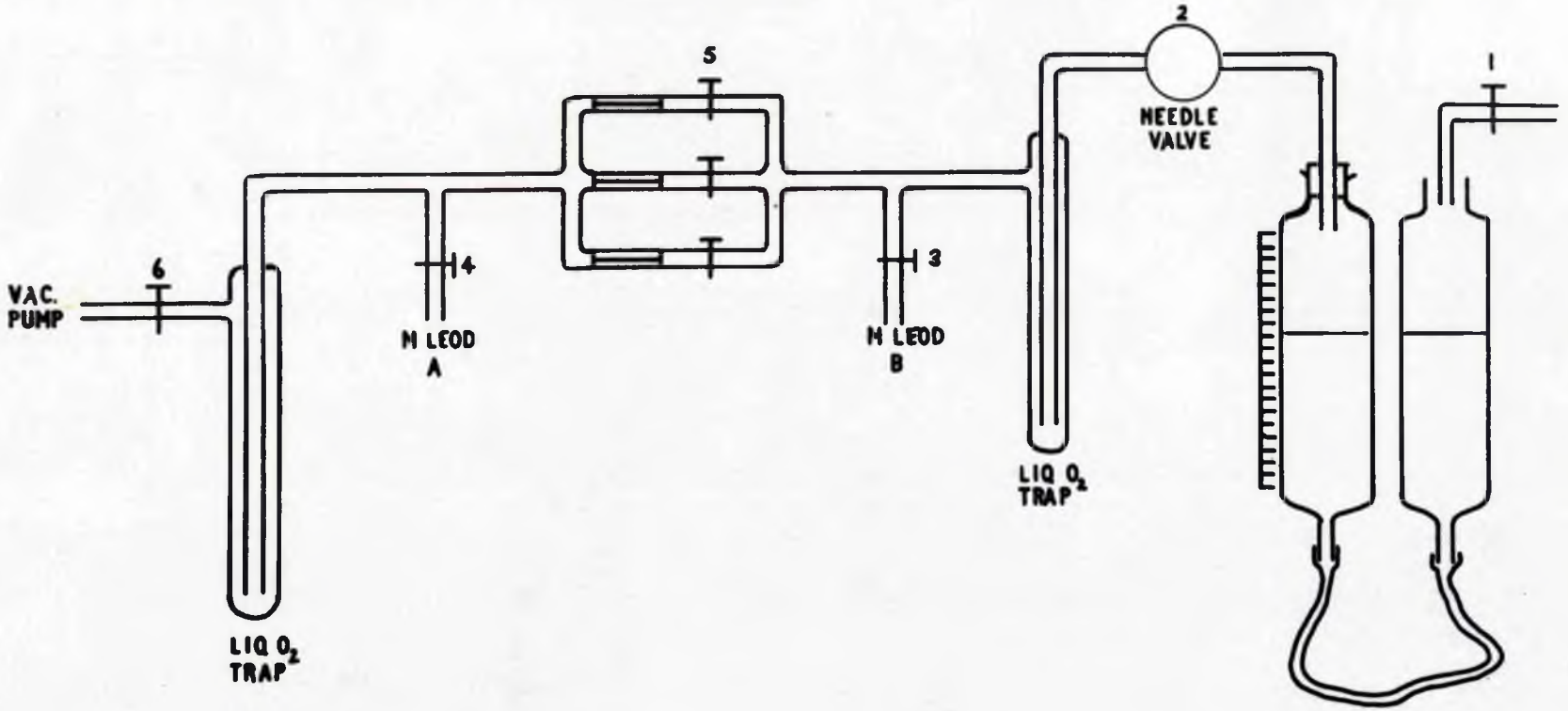


Fig. 4.

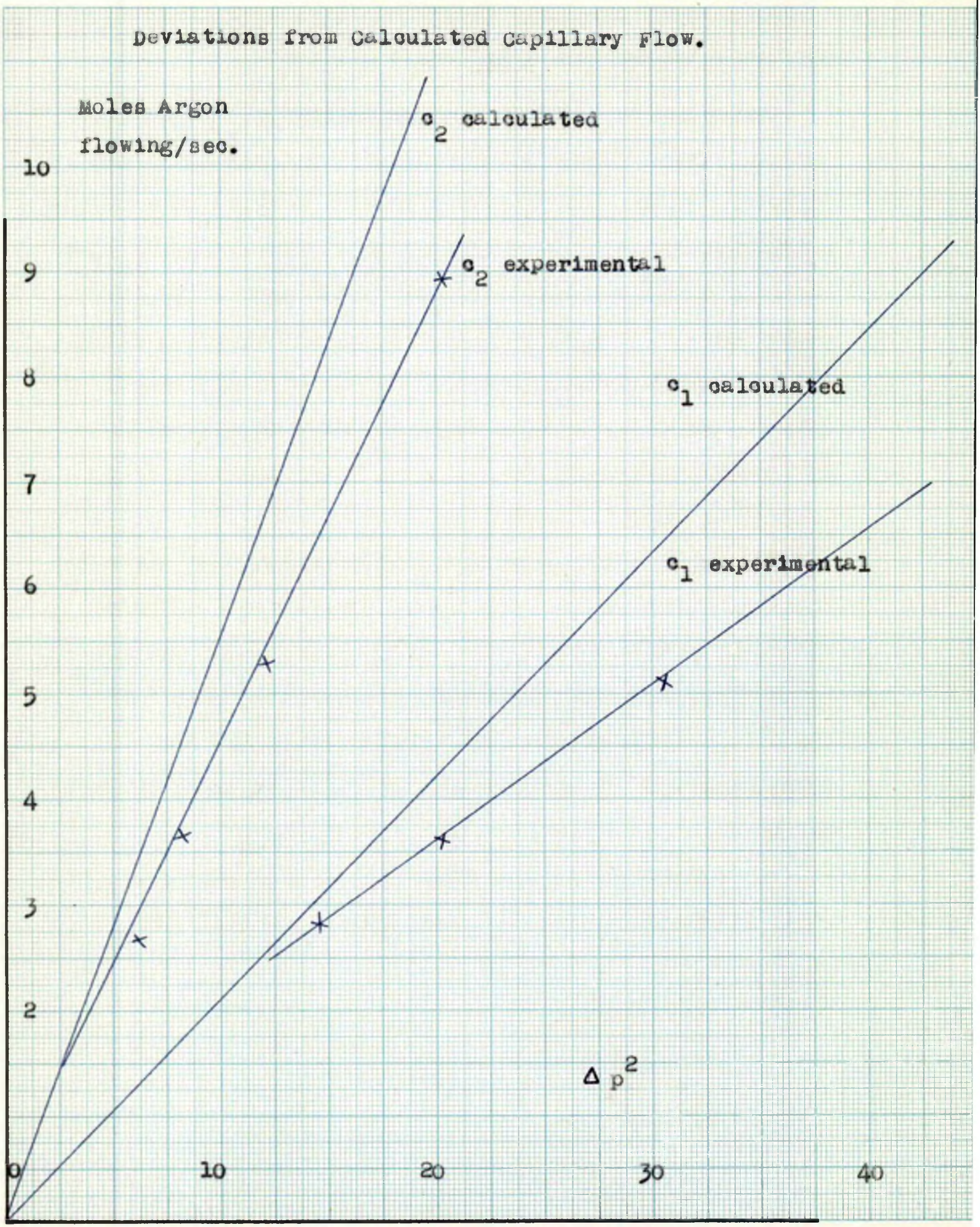

Deviations from Calculated Capillary Flow.
Moles Argon flowing/sec.
10
9
8
7
6
5
4
3
2
0
10
20
30
40
Δp^2
c_2 calculated
c_2 experimental
c_1 calculated
c_1 experimental

Fig.5.

This can be written $n = k (p_b^2 - p_a^2) = k \Delta p^2$

During work on a similar apparatus but with higher carrier gas pressures, Cowan[52] found that the calculated and calibrated rates differed. To check whether this occurred for the present conditions, calibrations were carried out with two of the flow capillaries used. The apparatus for capillary calibration was as shown on the diagram facing page 32 . A measured volume of dry air was pumped through the capillary at a constant rate and the time of pumping noted. The pressures across the flow capillary were maintained at about 2 mm by a needle valve between the air reservoir and capillary, and were measured by two McLeod gauges.

The graphs of rate of carrier gas flow against Δp^2 are shown facing p. 32 , and the deviation between calculated and calibrated flow rates at high values of Δp^2 can be clearly seen. For most of the flow experiments the carrier gas pressure was about 3 mm and $\Delta p^2 < 5$, so in practice, the deviation was small. The calibrations with dry air were corrected for the viscosity of argon[53] before use.

The capillaries were used separately, or in parallel combination, using the formula $k = k_1 + k_2$ to calculate the combined rate constant k.

The dimensions and constants of the capillaries used are given:

TABLE 4

Capillary	Const. k.	length (cm)	radius (cm)
C_1	2.13×10^{-6}	7.120	0.1240
C_2	5.47 "	6.955	0.1500
C_3	3.94 "	12.314	0.1656
C_4	0.50 "	8.946	0.0912

Reaction vessels.

For most of the flow reactions, a silica vessel with a re-entrant central thermocouple well was used (volume of heated portion 280 ml.). The heterogeneity test experiments were carried out with a pyrex furnace for ease of manipulation. Removable concentric liners were constructed so that the surface / volume ratio could be changed. For both vessels, the length of the heated portion was about 50 cm. (measured exactly after each "smoothing" of the furnace)

The Furnace.

This was an inconel tube covered with asbestos paper and a layer of alundum cement, and wound with nichrome tape. The winding was closer at the ends, and had four intermediate tappings as well as leads to the ends. Shunts across these tappings made adjustment possible so that, with a fixed A.C. potential across the ends of the

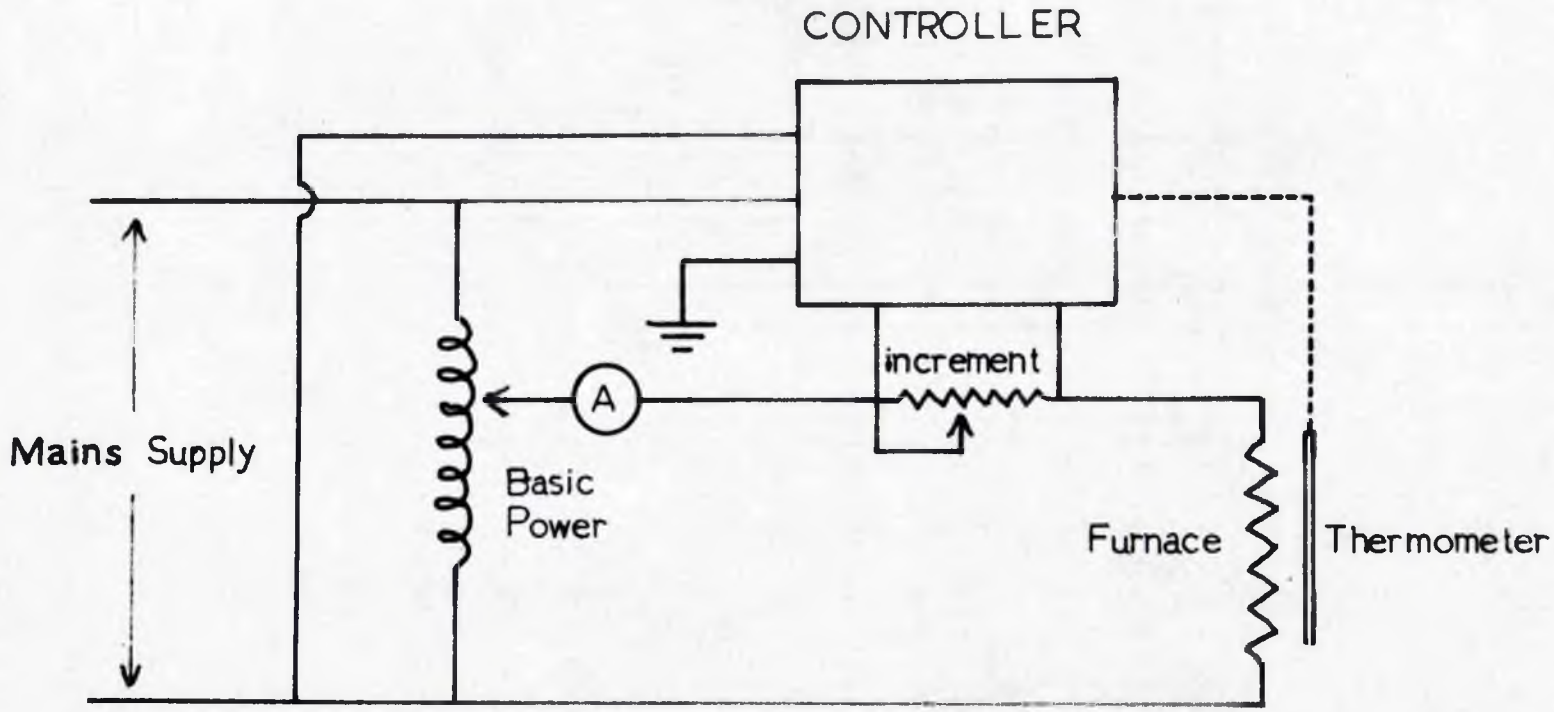

CONTROLLER
increment
A
Mains Supply
Basic
Power
Furnace
Thermometer

Fig.6.

furnace, the temperature was constant along its length to ± 1.5°C.

Temperature control.

A furnace controller of a type similar to the Sunvic RT_2 was constructed. This employs a platinum resistance thermometer, in an AC bridge circuit, to measure the temperature. At steady state, the bridge is balanced but when the furnace temperature changes, due to alteration in room temperature or change in the mains voltage, the out-of-balance signal from the bridge is amplified in two stages and relayed to a thermal cycling unit, which adjusts the furnace current to compensate. The circuit for the wiring of the controller and furnace is as shown opposite. The controller was capable of bringing the furnace temperature to the same value, on successive days, within ± 1°C. Throughout a single day, it controlled the mean temperature to within ± 0.5°C.

Temperature measurement.

This was done using a chromel-alumel thermocouple. The emf was measured on a direct-reading Pye potentiometer and the results were plotted against temperature. The thermocouple was calibrated against the melting points of pure tin (231.8°C), lead (327.4°C) and zinc (419.45°C) and found to agree with the literature data [54] within the limits of experimental error.

The Flow Lines.

To prevent the condensation of benzil and involatile products on the walls of the flow lines, these were lagged and maintained at about 120°C where necessary with nichrome tape electric heaters.

Injection of the reactants.

Benzil.

In the toluene carrier technique as developed by Szwarc, and as applied by Jaquiss to the decomposition of benzil, the reactants are introduced by passing the stream of carrier gas (in these cases, toluene vapour) over a U tube containing the reactants. To start the reaction, a heated bath at the required temperature is raised round the reactant.

A great source of error in this method is possible solution of toluene in the reactant, altering its effective vapour pressure and hence making erroneous the calculations involving the amount of reactant passing through the furnace in a given time. Also, since the U tube and contents take a little time to come to temperature, the start of a reaction is not clearly marked, and cooling of the U tube does not give an instantaneous end to the reaction. These difficulties can be avoided by using an injection capillary and valve. A much higher pressure of reactant than that required in the flow stream can be maintained behind the injection capillary, thus preventing back diffusion of toluene vapour during injection, and the time of injection can be closely controlled by opening and closing the valve.

To obtain a reasonably constant rate of benzil injection independent of small variations in the 2mm carrier gas pressure,

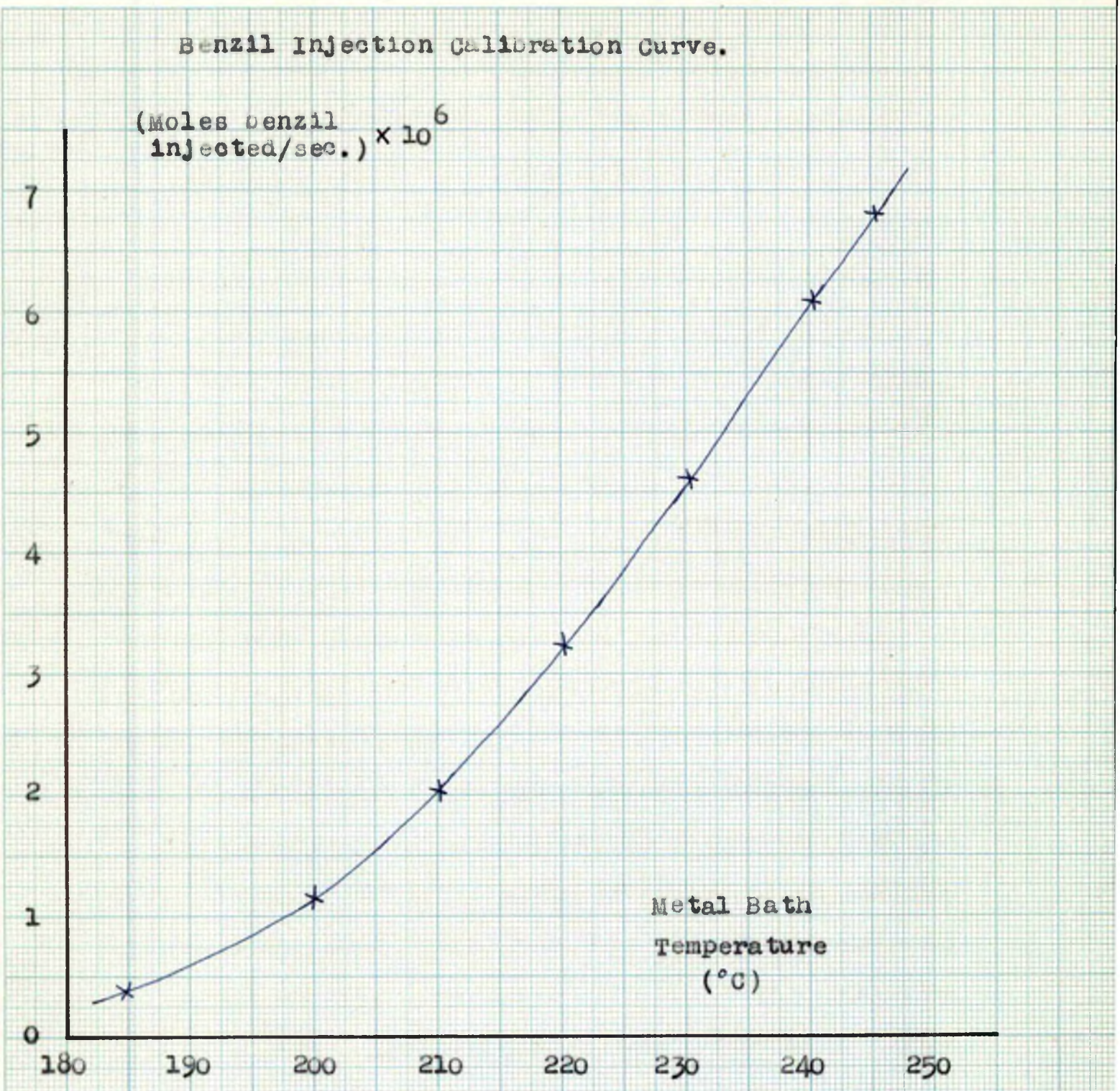

Benzil Injection Calibration Curve.
(Moles benzil injected/sec.) x 10^6
7
6
5
4
3
2
1
0
180
190
200
210
220
230
240
250
Metal Bath Temperature (°C)

Fig. 7.

the pressure of benzil vapour behind the injection valve should best be kept above about 15 mm, and this required a benzil temperature of about 200°C. To prevent condensation in the valve its temperature should be higher, so the requirements for the valve were that it should be vacuum-tight, that it should not cause decomposition of the reactants, and that it should withstand prolonged heating to about 250°C. A valve to meet these specifications was specially constructed, and is described in the appendix. The benzil container was maintained within ± 0.4°C at temperatures near 200°C by a lead - tin solder bath with a Fenwall temperature controller and two heaters, one steady, one controlled.

Unfortunately, since the valve was at about 250°C to prevent condensation, at this temperature slight decomposition occurred at the brass injection capillary, and the resulting blockage caused slightly irregular delivery. The benzil delivery was, therefore, checked by analysis of the products for each experiment. In addition, and to facilitate calculation of the expected benzil injection under certain conditions, the injection system was calibrated by measuring the benzil delivery with the furnace at about 120°C. A sample calibration curve is shown opposite.

Toluene.

A valve similar to that for benzil was used for toluene injection. The toluene container was maintained within ± 0.2°C at 10-70°C in a water bath fitted with dual heaters and a Fenwall temperature

controller. The delivery was reproducible within about 3% and was measured accurately for each experiment.

Measurement of furnace pressure.

To determine the contact time, the pressure in the furnace was required. Simultaneously with the calibrations to find the optimum circulation pump bath temperature, experiments were carried out to measure the furnace pressure p_p. An extra line, with an intermediate liquid air trap to catch toluene, was connected between a two-way tap at one of the McLeod gauges (B) and the entrance to the reaction furnace. 2 mm. argon were circulated round the apparatus, which was lagged and heated as for a run, and toluene was injected into the carrier stream. With the optimum circulation pump conditions for that temperature the pressures were measured at the furnace inlet, at the circulation pump outlet trap 2, and at both sides of the flow capillary. This calibration was repeated at varying carrier gas pressures, with different flow capillaries and injecting varying amounts of toluene.

The measured pressures were found to be related by an expression of the type:

$$P_p = p_b + K(p_c - p_b)$$

where P_p = furnace pressure
p_b = pressure before flow capillary
p_c = pressure at circulation pump outlet
K = a constant which varies only with the amount of toluene injected.

A calibration plot was obtained for K against the temperature of the water bath round the toluene container.

Collection of the products.

Four traps (F) were arranged in parallel so that four experiments could be performed for one evacuation of the apparatus. For experiments with toluene addition, the flow was directed through one trap at a time by means of cut-offs consisting of stainless-steel balls in ground glass seats, which could be adjusted with a magnet. The traps were internally heated so that involatile products came to the bottom of the trap and were easily removed. The coolant used on these collection traps varied with the nature of the experiment, as did the method of separation of the products. Subsidiary traps G allowed for the distillation of the more volatile products from the heater traps F.

Preparation and Purification of Reactants.

(1) Benzil.

The starting material was benzil from British Drug Houses Ltd. Two methods were used for purification:

(a) Re-crystallisation from ethanol. This was repeated until the melting point was sharp and constant at 94.5°C, and usually four treatments were required.

(b) Fractional freezing. A long, narrow (7.5 mm diam.) glass tube containing benzil was lowered slowly (about 2 cm / hour) through

TOLUENE PYROLYSIS APPARATUS

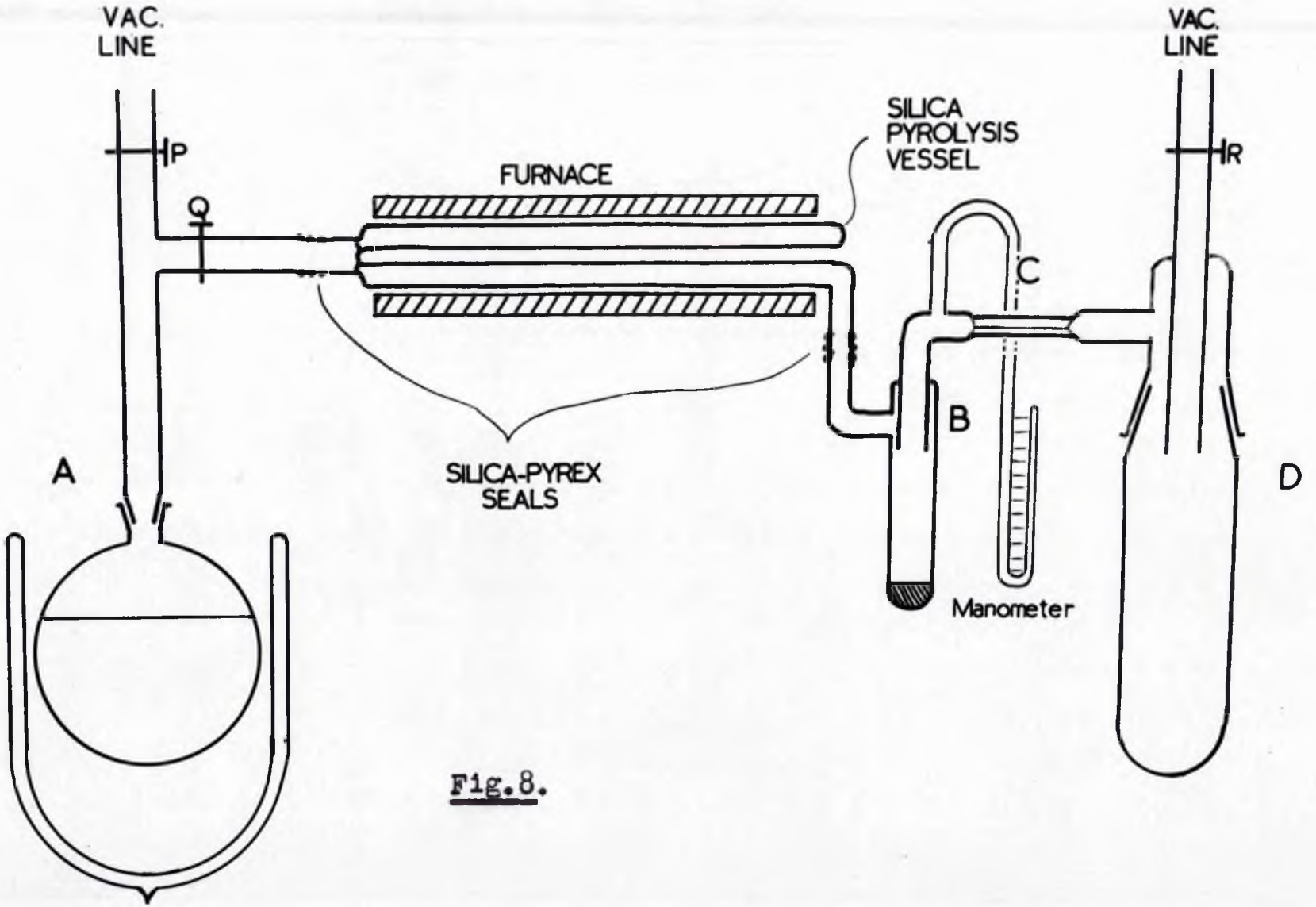


Fig.8.

a tube heater at a temperature just above the melting point of benzil into a thermostatically-controlled oil bath at a temperature just below the melting point. Impurities tend to stay in the liquid phase and can be decanted. Three successive treatments gave a product with as sharp a melting point as that from four times recrystallisation from ethanol. The U.V. spectrum was checked against the literature data.[53]

(2) Toluene.

Sawers[7] found that treatment by shaking with sulphuric acid, distillation, and crystallisation, still left impurities causing side reactions on pyrolysis. He found that these impurities could be removed by partially pyrolysing twice at 865°C, and by fractionally distilling over sodium. For these experiments, toluene from British Drug Houses was shaken with concentrated sulphuric acid until successive additions of acid were no longer coloured, washed with water, dried over calcium chloride and partially pyrolysed at 860°C, using a contact time of about 0.5 sec. (a diagram of the apparatus is shown opposite). The vapour pressure of toluene during the pyrolysis was controlled by adjusting the temperature of the water bath round the toluene flask. The product of the pyrolysis was again washed with sulphuric acid until the mixture was colourless, washed with water, dried over calcium chloride, and distilled from sodium through a column about 30 inches long and 1.5 inches wide, packed with Fenske rings. The fraction boiling over 0.2°C was collected. In the

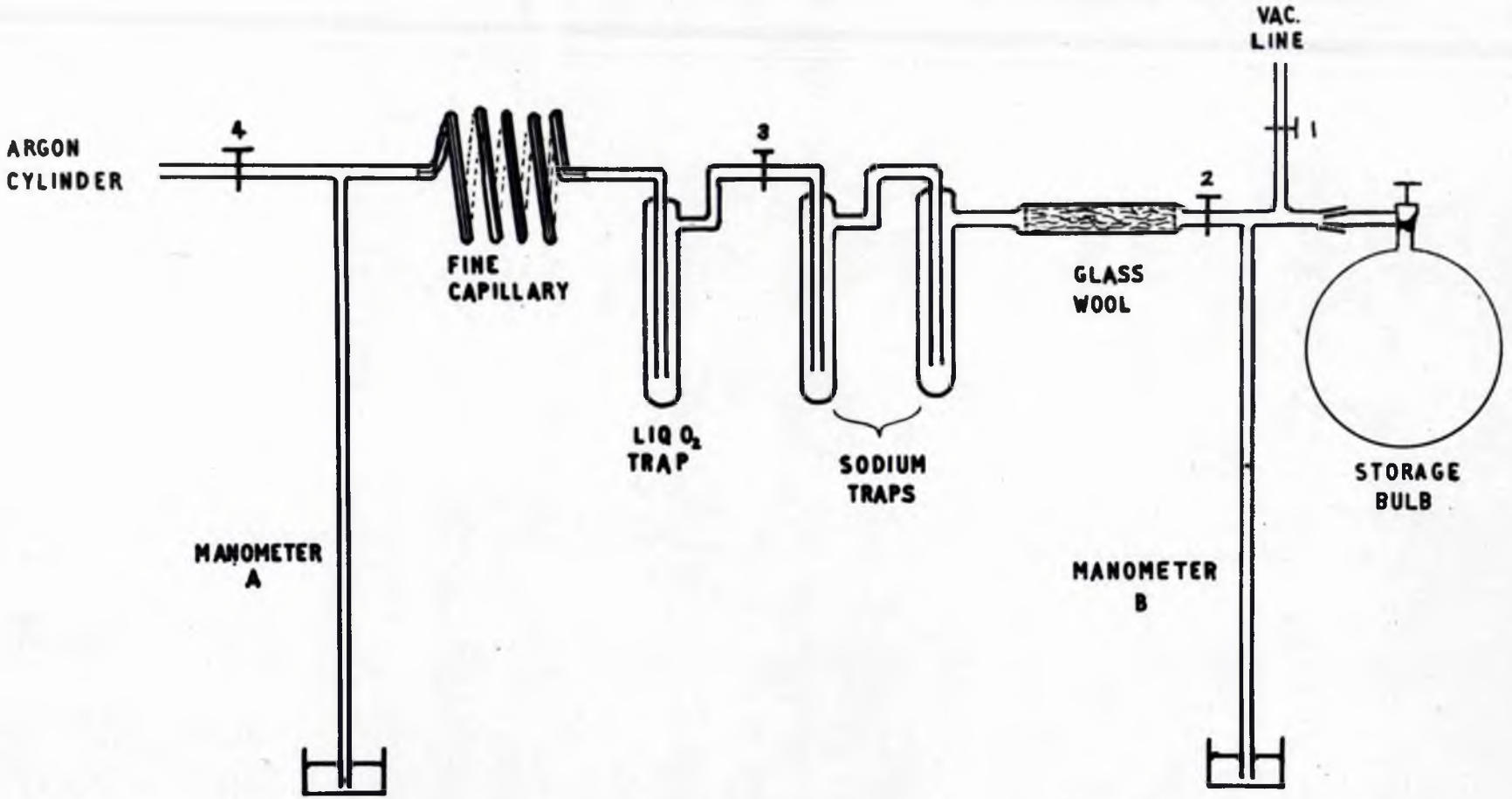

VAC.
LINE
ARGON
CYLINDER
4
3
2
1
FINE
CAPILLARY
LIQ O_2
TRAP
SODIUM
TRAPS
GLASS
WOOL
STORAGE
BULB
MANOMETER
A
MANOMETER
B

Fig.9.

PREPARATION OF CARBON MONOXIDE

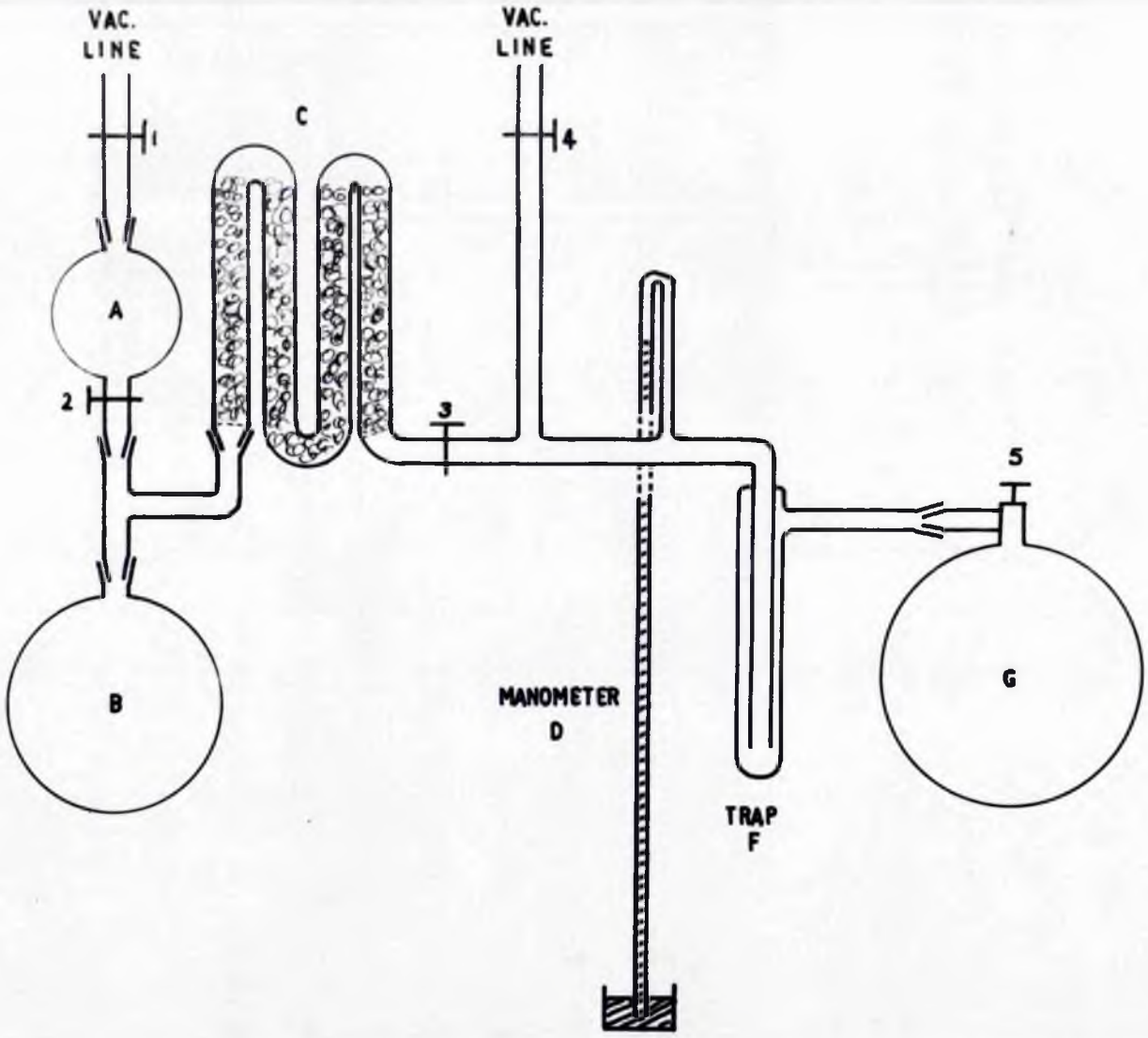


Fig.10.

subsequent experiments no difference in behaviour was noticed between samples which had been pyrolysed once or twice.

(3) Argon.

As the diagram of the apparatus (opposite) illustrates, argon at 1 atm. pressure could be passed very slowly over a liquid air trap to remove water, and over sodium at 300°C to remove oxygen. The flow was so controlled that the filling of a 5 l. flask took about 2½ hours.

(4) Hydrogen.

To remove any oxygen present, the hydrogen, at one atmosphere pressure, was passed over platinised asbestos at 200°C to catalyse the combination of any oxygen present with the hydrogen to form water, and through a liquid air trap to remove the water. The apparatus used was otherwise rather similar to that for argon purification.

Carbon monoxide preparation.

For calibration purposes pure carbon monoxide was required. A diagram of the apparatus used for its preparation is as shown opposite. 60 gm. concentrated sulphuric acid were placed in flask B, and 20 gm. analar (90%) formic acid in funnel A. The acids were de-gassed free of air by pumping through tap 1, and warming gently. The rest of the apparatus beyond tap 5 was pumped out to 10^{-5} m mercury. Formic acid was dripped slowly (to prevent frothing) into the sulphuric acid at room temperature and the reaction controlled by warming or cooling flask B. The anhydrous caustic potash in column C held back any acid distilling over and dried the carbon

GAS BURETTE

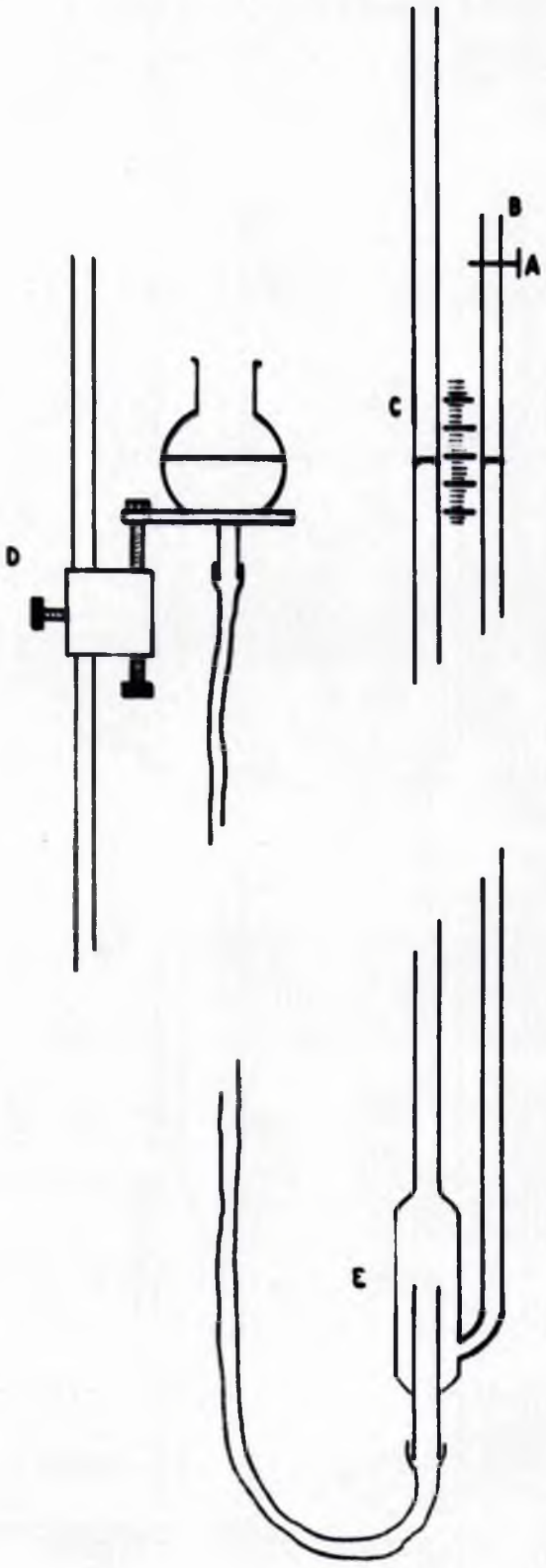


Fig. 11.

monoxide. The flasks E (total volume 8 l.) were filled to about 700 mm. pressure. A mass spectrometer check showed the gas to be oxygen free.

Deoxybenzoin.

An early method of preparation[56] was by the reduction of benzoin with zinc and glacial acetic acid. Cleaner products were obtained by the two-stage synthesis via phenacetyl chloride.[57]

$$5\ C_6H_5\ CH_2\ COOH + PCl_5 \longrightarrow 5\ C_6H_5\ CH_2\ COCl + H_3PO_4$$

$$C_6H_5\ CH_2\ COCl + C_6H_6 \xrightarrow{[AlCl_3]} C_6H_5\ CH_2\ CO\ C_6H_5 + HCl$$

The product was purified by repeated recrystallisation from methanol to a constant, sharp melting point.

Analysis of the Products.

Carbon monoxide.

(a) It was originally intended to measure this with the mass spectrometer and provision was made for introducing the mass spectrometer leak into the flow line by opening two greaseless mercury cut-offs. Several measurements were performed in this way, the mass spectrometer being calibrated on each occasion by the injection of measured amounts of carbon monoxide from the gas burette (see diagram opposite) into the circulation line. General demands for the use of the mass spectrometer and the difficulty of operating it at the same time as the flow apparatus rendered the method unsatisfactory.

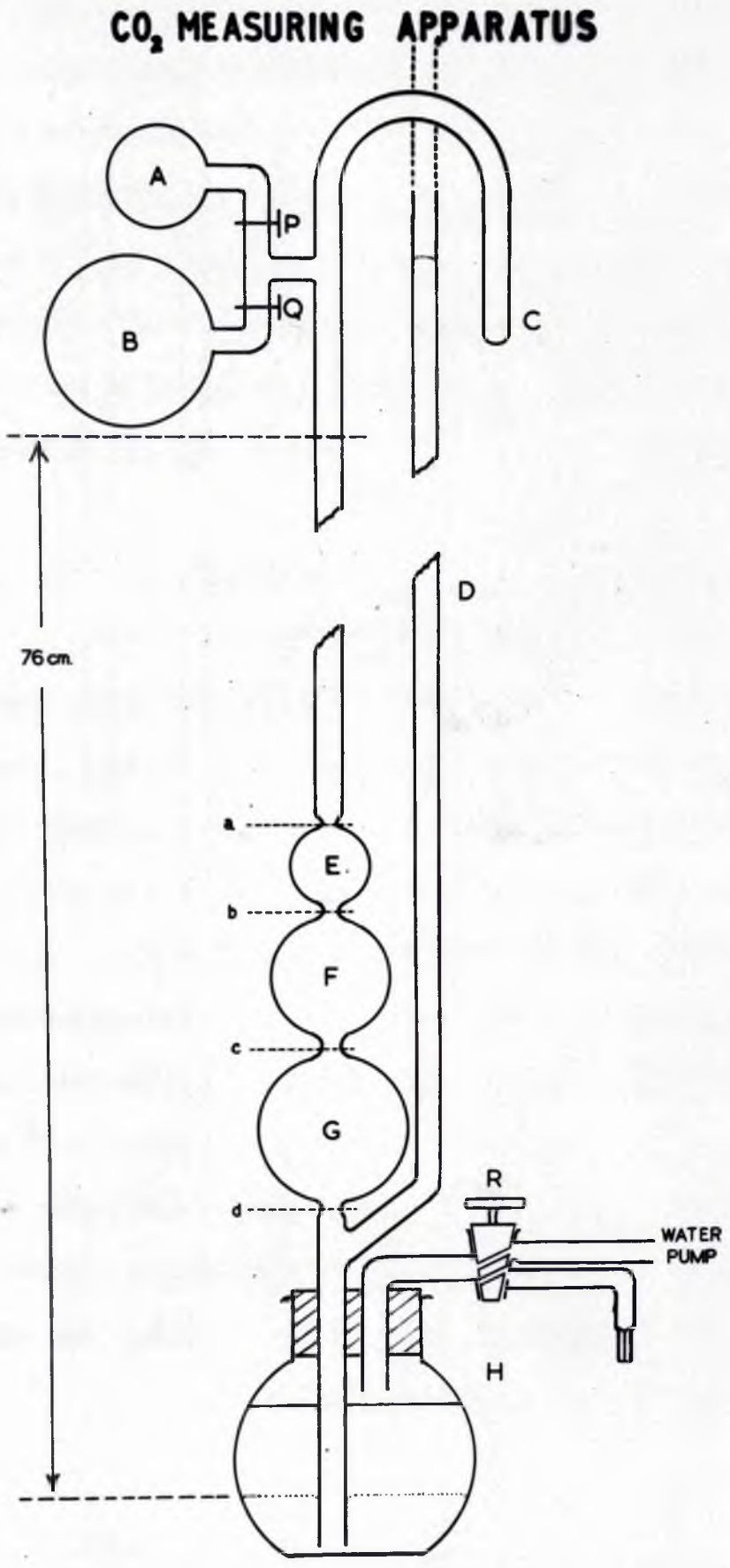


Fig.12.

(b) For the bulk of the experiments, the carbon monoxide was oxidised to carbon dioxide by passing repeatedly over cupric oxide at 400°C. In fact, one passage over the 4 feet long furnace ensured almost complete oxidation to carbon dioxide, and this was collected over liquid oxygen in the trap M. The liquid oxygen cooled trap S prevented any toluene reaching the cupric oxide and being oxidised. The carbon monoxide was measured in the device of which a diagram is shown opposite page 42. This is a modification of an apparatus used by Le Roy.[58]

The limb D was connected to the trap M (in the main apparatus diagram). Liquid oxygen was placed round the limb C, the mercury was drawn down into the reservoir H by the water pump, and the liquid oxygen bath was removed from the trap M. The carbon monoxide distilled through the measuring apparatus into the limb C completely in 15 minutes. Air was allowed to enter the reservoir H by the tap R, and the mercury rose to trap the carbon monoxide, which was then allowed to volatilise. The mercury level in the left-hand limb was adjusted to one of the levels a,b,c,d by suction on the reservoir H, and the difference between the standard mark (a,b,c or d) and the level in limb D measured. Since the volumes of the left-hand limb above the levels a,b,c,d were known, the amount of carbon dioxide could be calculated. For larger amounts of carbon dioxide, the subsidiary standard volumes A, B could be connected.

For some experiments measurements of the hydrogen produced were required, and cupric oxide at 400°C readily oxidises hydrogen to water. Iodine pentoxide has been used[59] for analytical purposes as a specific oxidant for carbon monoxide.

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

The cupric oxide furnace was replaced with one packed with iodine pentoxide. With this furnace at 200°C the oxidation was found to be slow and the method inconvenient. Much higher temperatures could not be used as iodine pentoxide decomposes rapidly at about 350°C.

$$2\ I_2O_5 \longrightarrow 2\ I_2 + 5O_2$$

Toluene.

This was usually separated from the involatile product by distillation into the subsidiary traps C, cooled by liquid oxygen, from the main trap at about 20°C, and was then estimated by weighing.

Benzene.

Benzene distilled over with the toluene and was usually present as less than 5% (by gm. weight). The analysis of benzene in this mixture was carried out on the mass spectrometer by the peak ratio method.[60] The mass spectrum of benzene has a strong peak at mass 78 ($C_6H_6^+$), whereas the toluene spectrum shows strong peaks at masses 91 and 92, and a relatively small contribution at mass 78.

Two approaches could be made to the analysis:

(a) the volts response (peak height) at mass 78 could be expressed:

$$V_{78^+} = f(C_6H_6) + f'(C_7H_8)$$

and at mass 91 $V_{91^+} = f''(C_7H_8)$

Hence, it should be possible to calculate the composition of a mixture from measurements of the peak heights at masses 78 and 91 if the heights of the two peaks in pure benzene and toluene were known.

(b) A simpler method is to construct an arbitrary calibration graph by measuring the mass 78 and mass 91 peak heights for standard mixtures of benzene and toluene, and plotting composition against peak ratio. Hence, the composition of the mixture can be calculated directly from measurement of the mass 78/91 peak ratio.

The results for a full calibration are tabulated below:

TABLE 8

Mixture	Peak Height (Arbitrary units of volts reading on instrument) 78	91	78/91	corrected 78/91
pyrolysed toluene	0.0065	0.712	0.77	
50% benzene in toluene	0.176 0.173	0.320 0.318	55.0 56.0 av.55.5	54.75
20%	0.128 0.122	0.365 0.350	35.0 34.8 av.34.9	34.15
10%	0.064 0.065	0.402 0.402	15.90 15.70 av 15.80	15.05

Benzene Analysis Calibration.

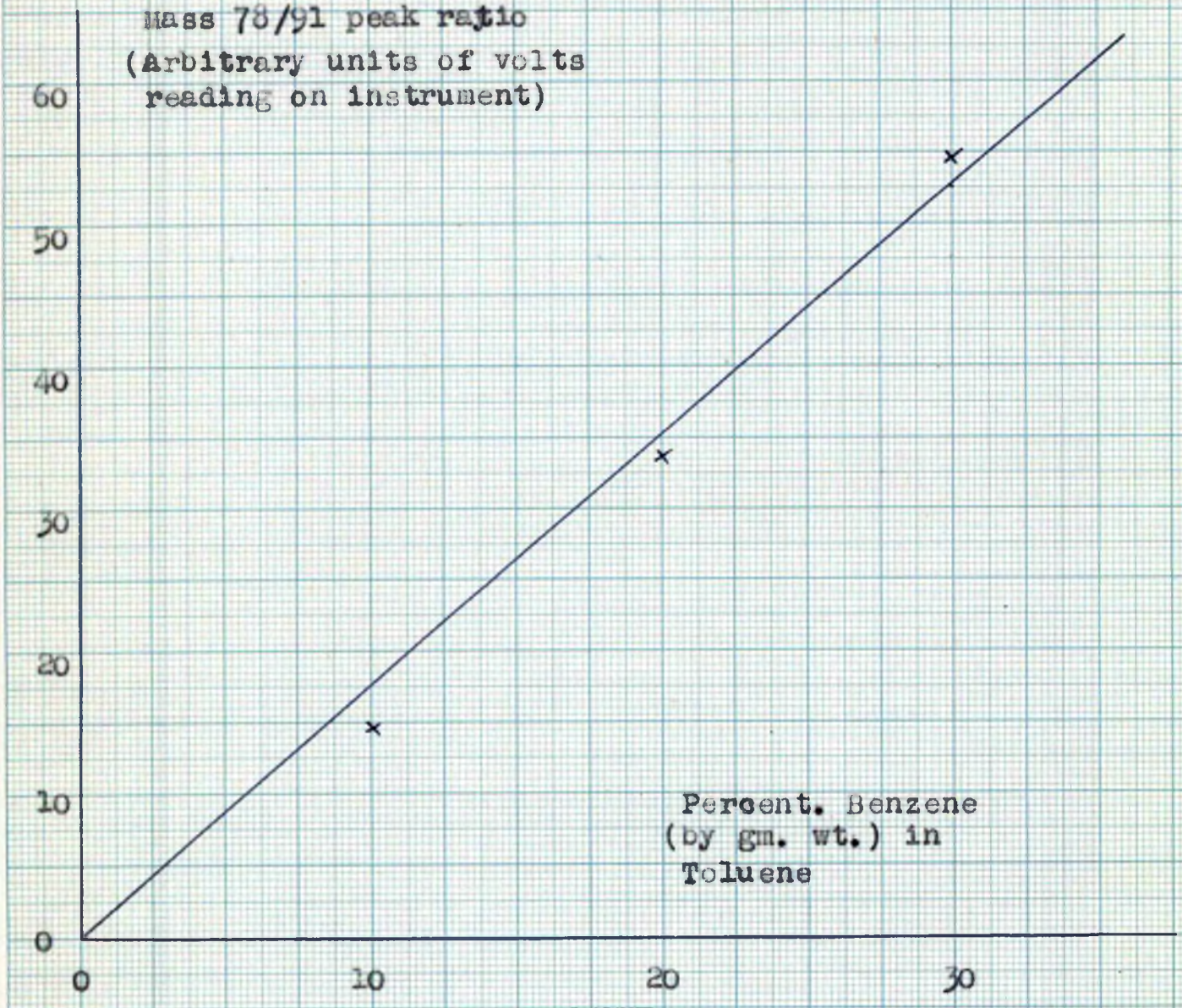


Fig.13.

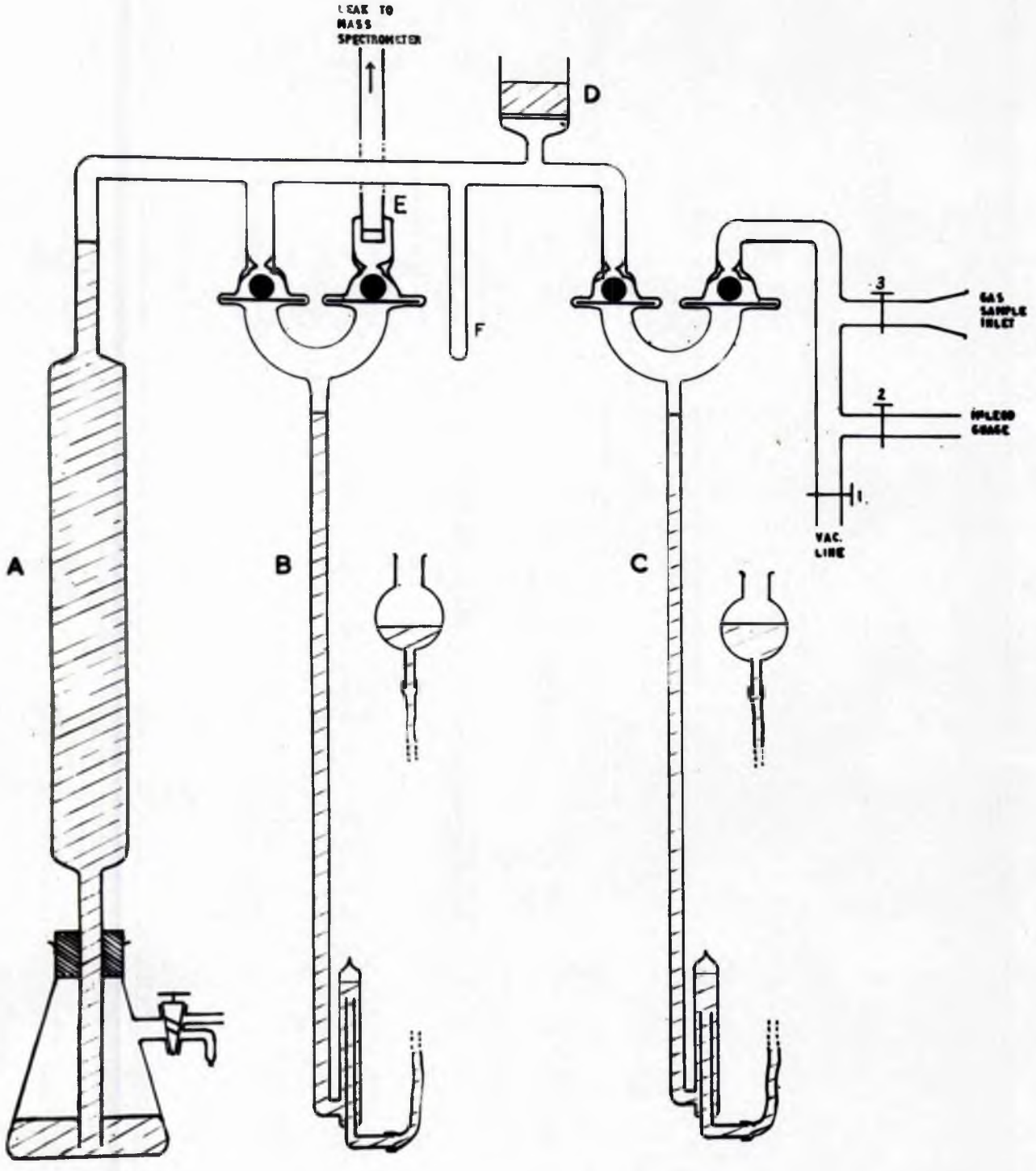

LEAK TO
MASS
SPECTROMETER
D
E
F
3
GAS
SAMPLE
INLET
2
MCLEOD
GAUGE
1
VAC.
LINE
A
B
C

Fig.14.

MICROBURETTE

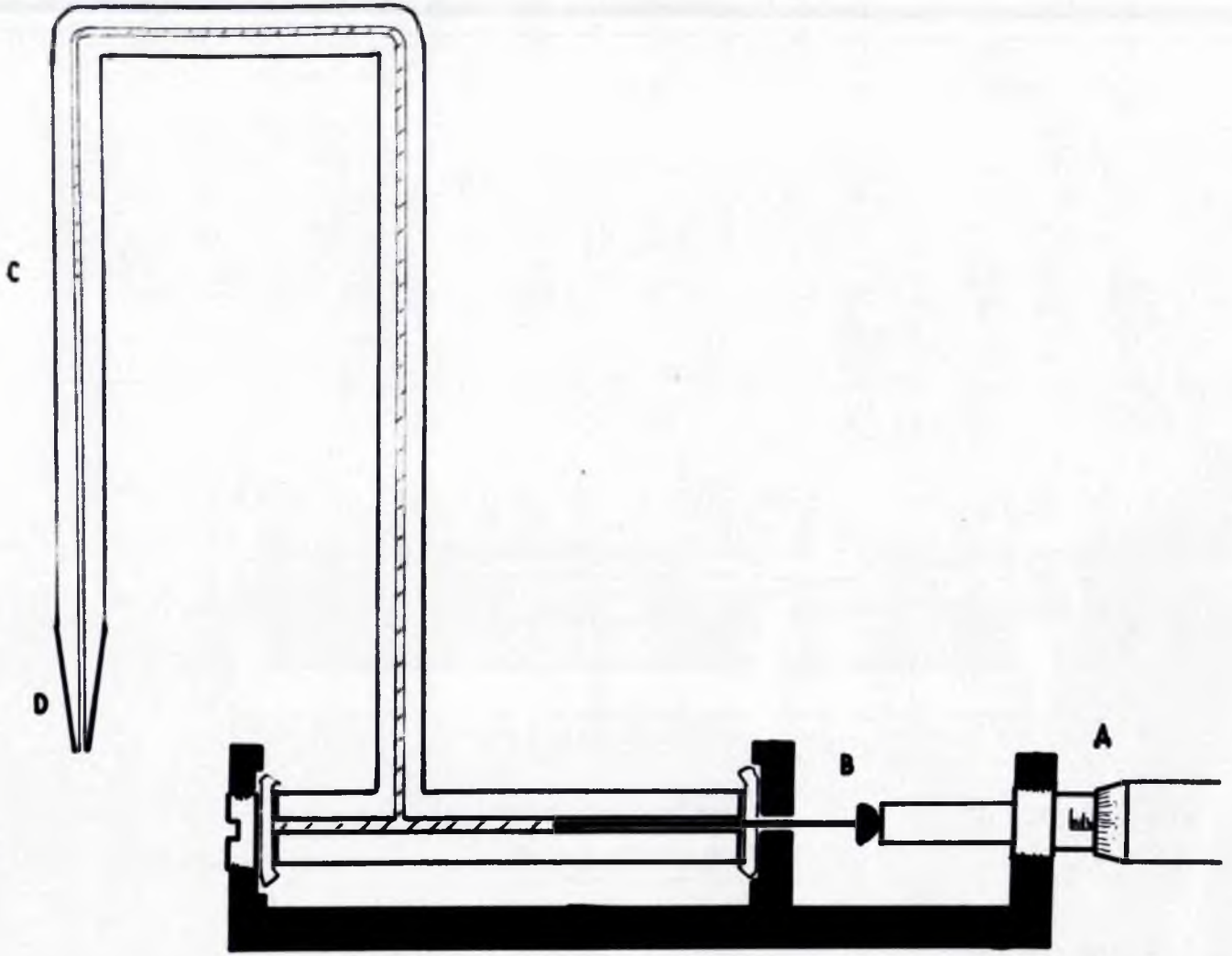


Fig.15.

A plot of the results is shown opposite and the scatter is seen to be about 5%. Checks with other standard mixtures showed that the composition would be estimated within 5% error.

The mass spectrometer used had no temperature control in the ionisation region and possibly as a result of this showed a rather variable cracking pattern for the same mixture. Barnard [51] states that recent mass spectrometers have temperature control to ± 0.1°C, whereas the temperature of our instrument head varied over one or two degrees. To correct for this instability, a calibration with a standard mixture was carried out before each batch of analyses.

The mixture samples were introduced into themass spectrometer handling system (shown diagrammaticallly opposite) through the mercury/ sinter cut-off D, by a microburette. By raising and lowering the mercury in the vessel A, with cut-off B lowered, good mixing was ensured. A diagram of the microburette used is shown opposite. When pin B of the microburette is retracted, the mercury thread (shaded) also retracts and will draw in a sample of the mixture through the nozzle D. With the nozzle D in contact with the porous sinter on the handling system, measured rotation of the micrometer A causes injection of known amounts of the mixture (since the displacement of the pin B is known.)

Hydrogen.

This was measured by the rise in the mass 2 peak when the carrier gas stream was inspected by the mass spectrometer before

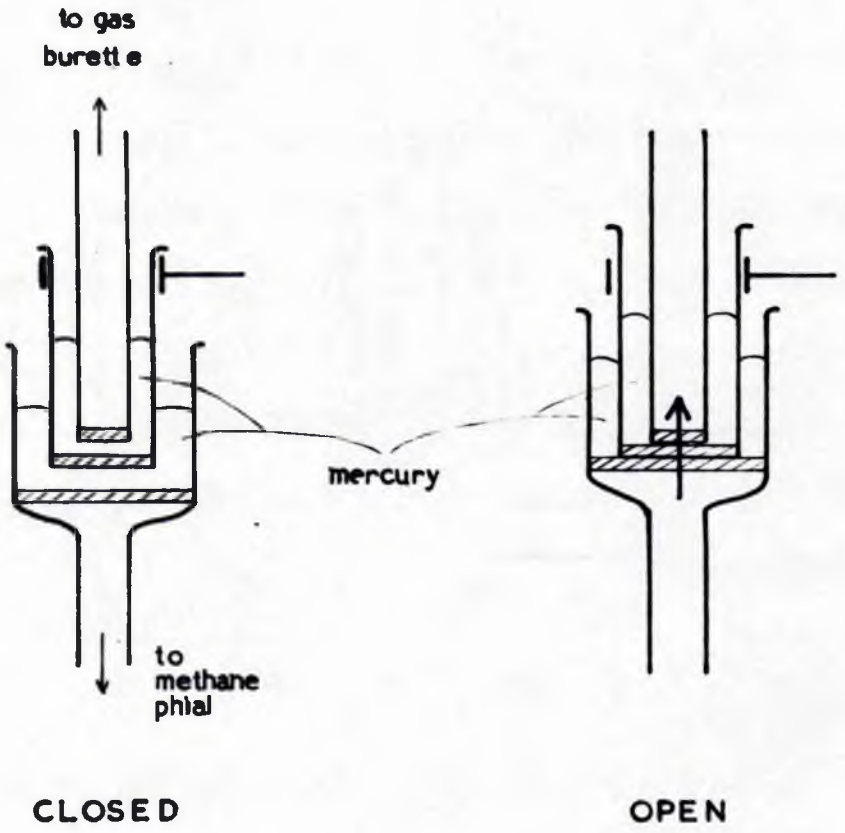


Fig.16.

and after an experiment. Calibration was carried out by measurement of the mass 2 peak rise when measured amounts of hydrogen were injected from the gas burette directly into the carrier gas stream.

Methane.

This was measured in a similar way to hydrogen by measurement of the mass 16^+ peak rise. Methane for calibration was bought in phials under a glass break-seal and was stored under a mercury/sinter cut-off. (since tap grease absorbs methane strongly). The gas was introduced to the calibration burette through a greaseless mercury/sinter "tap" as illustrated opposite. The top two sinters were first pressed together under mercury to pump out air from the middle sinter. All three sinters were then pressed together and methane passed through into the evacuated gas burette.

Involatile products.

Complete ultra violet absorption spectra of the products from experiments with benzil decompositions in the presence of toluene, using less than 10% conversion, showed that although the benzil spectrum was slightly modified at the low wavelengths (about 250 mμ), there was no detectable alteration in the region about 360 mμ. Benzil has a small peak at 362.3 mμ and this was used for its analysis. Deoxybenzoin has no peak at about 360 mμ, and was analysed at its main absorption peak 245 mμ.

(a) Initially, attempts were made to separate the involatile products

chromatographically by eluting with petroleum ether from an alumina column. The bands were observed by their fluorescence under U.V. light. Unfortunately benzil, and carbonyl containing compounds of similar size and complexity, all have rather similar ultra-violet absorption curves, and it was possible that two closely placed bands could overlap, and not be separated by ultra violet analysis. Fluorenone, however, was detected in a fraction from one of the experimental products.

(b) Attempts were made to examine the involatile products by reference U.V. analysis.[62] For this a benzil solution was placed in the reference cell, and its concentration varied until the benzil absorption in the test solution was just cancelled. The resulting absorption curve was due only to the absorption of the other products. Since benzil is in large excess in the products, the exact cancellation of its absorption is difficult, and the similarity of the U.V. absorption curves for possible carbonyl containing products makes the interpretation of the resultant absorption curve in terms of the composition of the mixture difficult.

(c) Towards the end of the research period an infra-red spectrometer became available. Since the carbonyl absorption band position is very sensitive to the type of structure in which the carbonyl group occurs, this instrument was very useful for the qualitative separation of the products. A reference technique was used here too, to reduce the effective absorption of the large excess of benzil present.

Iodine.

This was estimated by titration with N/10, N/100 or N/1000 sodium thiosulphate as appropriate, using starch indicator.

Hydrogen iodide.

This was first oxidised by bromine to iodate in a buffered acetic acid-acetate solution,[63] and then estimated by titration of the free iodine produced in the oxidation of potassium iodide by the iodate.

Description of an experiment.

(Letters are used in the following description to indicate sections of the apparatus in the diagram facing page 30).

The apparatus was first pumped out with the furnace, valves and circulation lines all hot, and a solid carbon dioxide-acetone bath at 30°C on the traps P,Q,R. The benzil was out-gassed by melting with the valve closed (when dissolved gas came out of solution), cooling to room temperature, and pumping through the valve. The toluene was out-gassed similarly but cooled to -80°C instead of room temperature. The process was repeated carefully until there was no further trace of evolved gas, as the decomposition of benzil was noted to be quite sensitive to even traces of oxygen. The circulation line was then isolated, argon carrier gas injected from a manostat, and the circulation pump started. Liquid oxygen was placed round traps

J and S, and the oxygen was circulated for at least 30 mins. over sodium (T) at 300°C to remove traces of oxygen, and over cupric oxide (K) at 400°C and the liquid oxygen traps J and S to remove any carbon monoxide or dioxide present. The sodium trap was then closed off, and the carrier gas flow directed through just one of the products collection traps F. A solid carbon dioxide-acetone bath was placed round this collection trap, and liquid oxygen round the carbon dioxide collection trap M. Flow conditions were adjusted by selection of the appropriate flow capillary and setting of the by-pass tap 15, and the furnace temperature and injection bath temperatures were checked and adjusted.

When conditions were steady, the toluene valve was opened and, two minutes later, the benzil valve. During the experiment the flow pressures and furnace temperature were measured at regular intervals. At the end of the experiment, the benzil valve was closed two minutes before the toluene valve to ensure that the benzil decomposed in excess toluene. The carbon dioxide was analysed as described, and pumped away. By altering the ball cut-offs and opening different collection traps three more experiments could be performed. The rate of injection of benzil was directly checked by collecting the amount injected over a measured time in the furnace by-pass trap H. The products were separated and analysed as already described.

Calculation of a velocity constant from the Experimental Results.

Squire and Jaquiss [1] assumed that the decomposition of benzil to carbon monoxide in presence of excess toluene, was first order. To test the kinetics a unimolecular rate constant was calculated on the basis of two molecules of carbon monoxide per unimolecular split, and the rate constant was given by

$$k = \frac{1}{t} \ln \frac{a}{a - X} \text{ sec.}^{-1}$$

where t = contact time

$$= \frac{\text{volume of reaction vessel in ml.}}{\text{total rate of flow through reaction vessel in ml/sec.}}$$

$$= \frac{\text{volume of vessel} \times p_p \times 273}{\text{average rate of flow over time of expt. in moles/sec.} \times 22400 \times T \times 760}$$

where p_p(mm) = average pressure in reaction vessel

T ($^{\circ}$K) = temperature of reaction vessel

a (moles) = total amount of benzil injected

X (moles) = half the amount of carbon monoxide formed.

The percentage decomposition was given by $\frac{100\ X}{a}$.

The partial pressures were calculated from the expression

$$\text{p.p.} = \frac{\text{moles of substance/sec.}}{\text{total moles/sec.}} \times p_p.$$

and the expression p_p = the sum of the partial pressures of all the substances in the furnace

For deoxybenzoin, X (moles) in the rate constant expression, was equal to the amount of carbon monoxide produced.

EXPERIMENTAL RESULTS.

TABLE 6

Expt.	partial pressure benzil	volts 28^+	moles CO	percentage decomp^{n}.	contact time (secs.)	Temp. (^oC)
(a)	(MS calibration 1.05×10^{-5} moles CO/volt 28^+)					
1	0.15	1.55	2.55×10^{-6}	0.196	0.67	524
2	0.15	2.47	4.07 "	0.315	0.66	527
3	0.15	2.76	4.60 "	0.357	0.67	528
4	0.125	2.60	4.30 "	0.355	0.66	528
(b)	(MS calibration 1.49×10^{-6} moles CO/volt 28^+)					
5	0.102	1.66	2.47×10^{-6}	0.246	0.72	525
6	0.105	2.57	3.83 "	0.361	0.72	527
7	0.107	1.19	1.77 "	0.352	0.73	528
8.	0.108	1.30	1.94 "	0.367	0.74	529
9	0.110	1.38	2.05 "	0.408	0.745	529
(c)	(MS calibration 1.46×10^{-6} moles CO/volt 28^+)					
10	0.16	2.20	3.20×10^{-6}	0.306	0.67	532
11	0.15	2.25	3.27 "	0.333	0.65	532
12	0.16	2.07	3.02 "	0.375	0.69	528
13	0.17	2.35	3.45 "	0.425	0.71	528
(d)	(MS calibration 2.40×10^{-6} moles CO/volt 28^+)					
14	0.17	1.50	3.60×10^{-6}	0.355	0.62	527
15	0.17	2.36	5.65 "	0.502	0.74	526
16	0.18	1.90	4.56 "	0.46	0.65	529
17	0.18	2.40	5.76 "	0.61	0.65	529

Thermal decomposition of benzil.

The first experiments were carried out with benzil alone, to test the analysis techniques, and to find the correct temperature region for 0-10 per cent. conversion. For these experiments the mass spectrometer was used to measure the carbon monoxide produced by following the 28$^+$ peak rise during an experiment. The results for these experiments are tabulated opposite.

Examination of each group of results a,b,c,d, performed on successive days, shows that the first experiments of groups a, b and d show a lower extent of decomposition than the others. For group c, a sample of benzil was passed through the apparatus before the experiments recorded were carried out. This increase of the percentage conversion to a steady value during a series of experiments may be due to a "seasoning" effect caused by the deposition of a layer of carbon on the furnace walls. Later tests showed that, for an experiment in the absence of toluene, carbon is deposited, and this carbon would be probably burned off at the end of each group of experiments when air was let into the hot furnace to remove the products for analysis.

The effect of toluene.

Several experiments were performed by injecting an excess of toluene along with the benzil and the results are tabulated below:

TABLE 7

Expt.	Temperature (°C)	contact time (secs)	partial pressure benzil (mm)	partial pressure toluene (mm)	Percentage decomposition
18	525	0.71	0.116	0.75	0.07
19	526	0.72	0.111	0.76	0.15
20	526	0.715	0.115	0.76	0.09
21	526	0.94	0.145	0.98	0.105
22	527	0.95	0.15	0.99	0.106

Mass spectrometer calibration = 2.27×10^{-6} moles CO/volt 28^{+}.

The furnace was not seasoned before these experiments and, though the results are rather scattered, the indication was that there was less effect due to lack of seasoning with excess toluene present than without it. Comparison of these results with those of group (b) in table 6 shows that the rate of decomposition to carbon monoxide drops by a factor of about three when toluene is added to the system.

A further series of experiments, at rather higher temperature, in only half of which toluene was used, confirmed these observations. The results are shown below.

TABLE 8

Expt.	Temperature (°C)	contact time (secs)	partial pressure benzil (mm)	partial pressure toluene (mm)	percentage decomposition
25	563	0.65	0.112	0	1.50
24	563	0.57	0.102	0.65	0.78
25	563	0.68	0.121	0	2.20
26	564	0.68	0.121	0	2.55
27	564	0.54	0.100	0.60	0.82
28	564	0.55	0.100	0.60	1.25

Mass spectrometer calibration 5.05×10^{-6} moles CO/volt 28^{+}.

Unfortunately, the mass spectrometer came into use for a variety of purposes, including solids analysis, and appreciable changes in its sensitivity were noted over quite short periods. Lack of temperature control in the mass spectrometer head may also have been a reason for changes in sensitivity over short periods.[61] The use of the mass spectrometer for carbon monoxide analysis was discontinued and another measuring device constructed,[58] as described in the previous section.

Using this more consistent method of analysis, experiments were performed with different partial pressures of toluene to notice the effect on the decomposition to carbon monoxide in detail. The results are shown below.

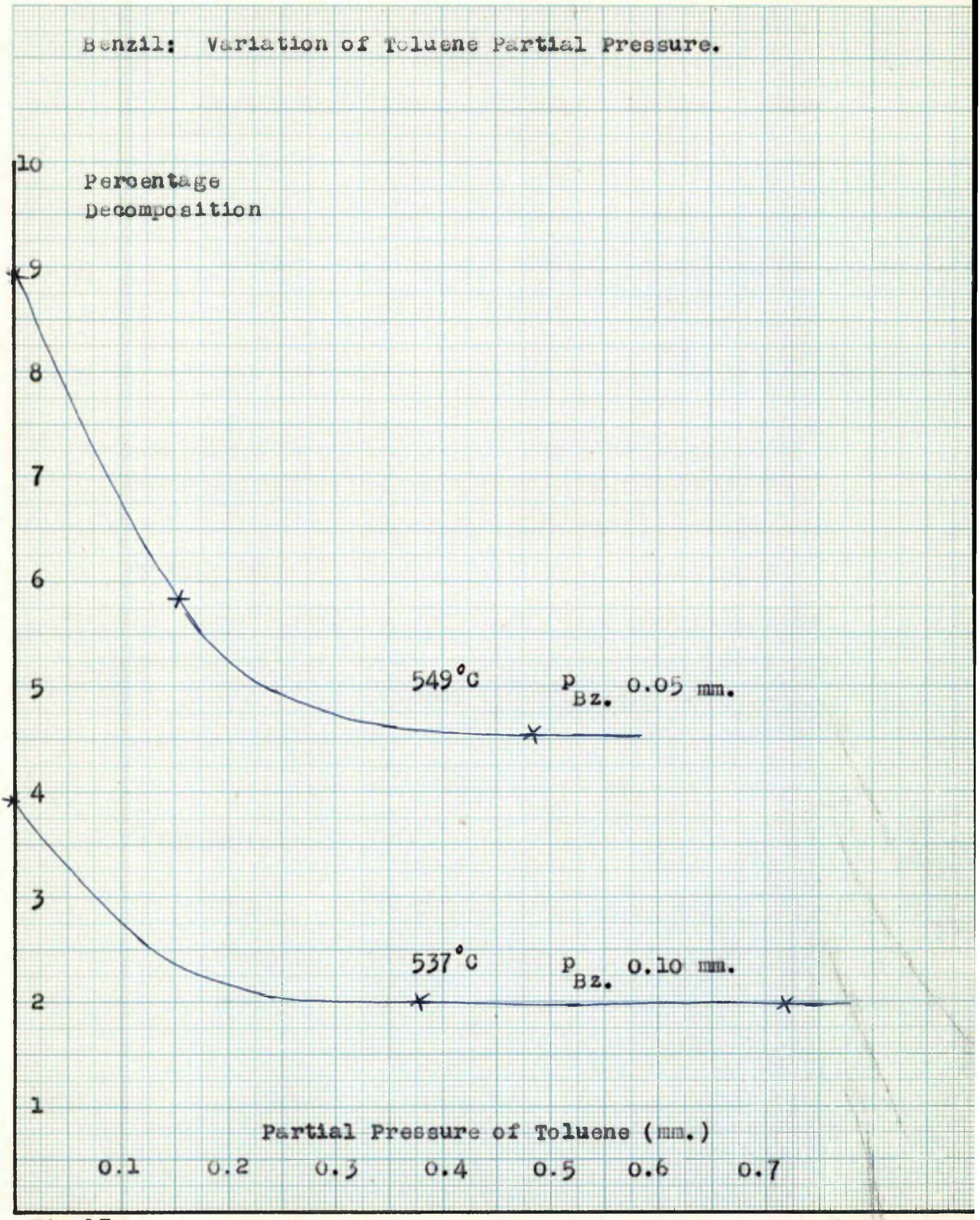

Benzil: Variation of Toluene Partial Pressure.
Percentage Decomposition
10
9
8
7
6
5
4
3
2
1
549°C
$P_{Bz.}$ 0.05 mm.
537°C
$P_{Bz.}$ 0.10 mm.
Partial Pressure of Toluene (mm.)
0.1
0.2
0.3
0.4
0.5
0.6
0.7

Fig.17.

TABLE 9

Expt.	contact time (secs)	partial pressure benzil (mm)	partial pressure toluene (mm)	percentage decomposition
29	0.65	0.06	0.95	2.10
30	0.65	0.045	0.72	1.95
31	0.71	0.050	0.37	2.03
32	0.72	0.040	0	5.90

(Experiments at 537°C).

If the figures for percentage decomposition and partial pressure of toluene are plotted, a sharp rise in percentage decomposition is noticed when no toluene is being used.

Three further experiments at a higher temperature (549°C) confirm that about a six times excess in partial pressure of toluene over benzil is sufficient, to stop whatever is the complicating reaction with no toluene present.

TABLE 10

Expt.	contact time (secs)	P_{bz} (mm)	$P_{tol.}$ (mm)	% decomposition
33	0.90	0.11	0	8.95
34	0.90	0.102	0.126	5.82
35	0.90	0.09	0.473	4.02

The plots of these data are shown opposite.

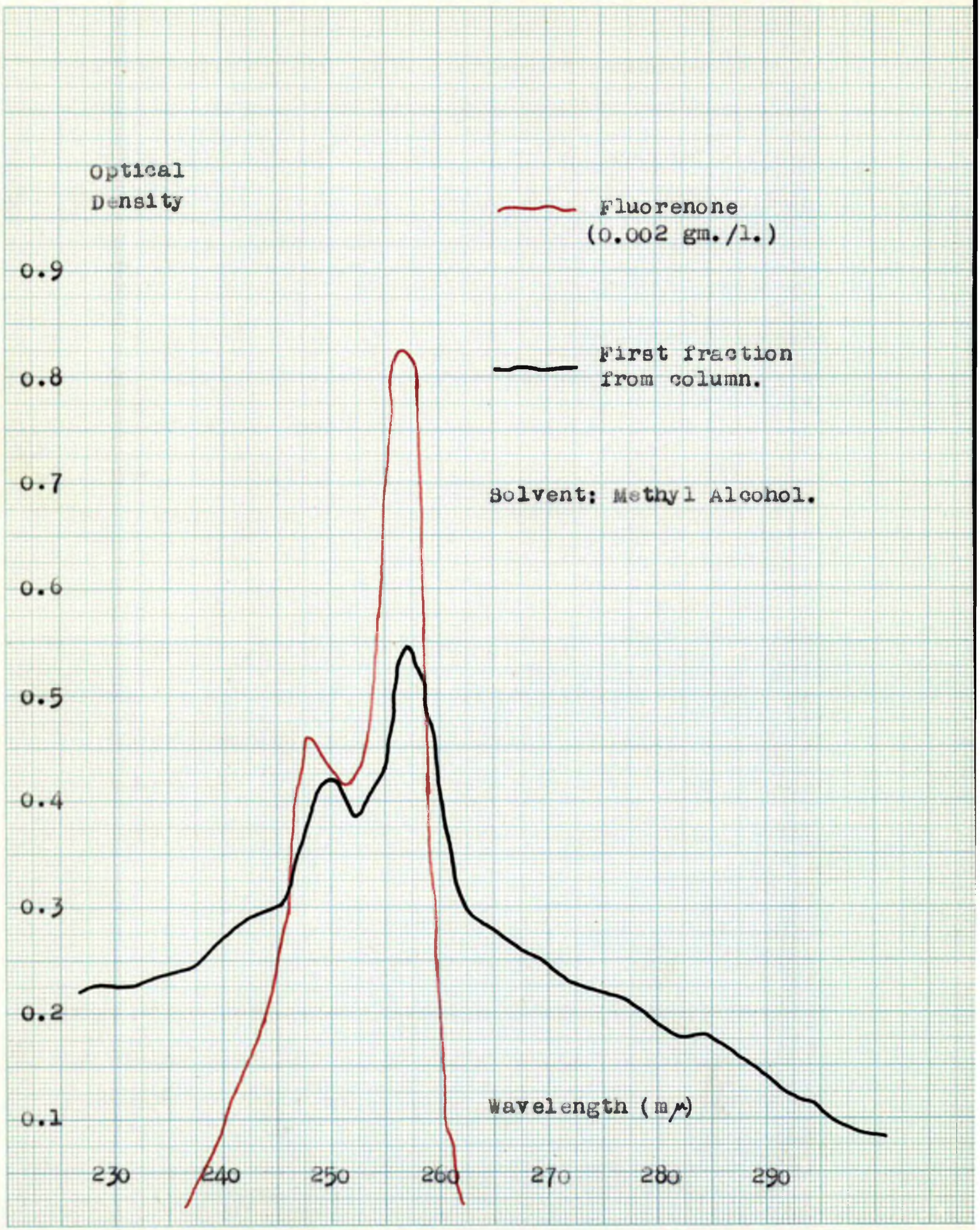

Optical
Density
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Fluorenone
(0.002 gm./l.)
First fraction
from column.
Solvent: Methyl Alcohol.
Wavelength (mμ)
230
240
250
260
270
280
290

Fig.18.

U.V. spectroscopic examination of the involatile products of the decomposition of benzil alone showed that these were not just a mixture of benzil and diphenyl. The products were taken up in petroleum ether, put on an alumina column, and eluted with mixtures of petroleum ether and benzene. Bands were visible under a U.V. lamp and the U.V. spectrum of the fraction containing the first fluorescent band showed the strong double peak of fluorenone. Copies of the spectra of this band and of pure fluorenone appear opposite. The width of the band on the column, and the shape of the absorption curve suggested that other substances were present in the band besides fluorenone. Later bands on the column showed no particularly characteristic spectra.

Later IR analysis, in carbon tetrachloride solution, of the products when benzil was decomposed alone showed the presence of both fluorenone and benzophenone. It also showed that the injection of excess toluene during an experiment eliminated them from the products, and, in this case, dibenzyl was formed. The presence of dibenzyl suggests that extraction of hydrogen fromtoluene takes place e.g. by phenyl

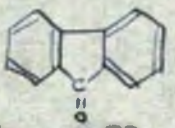
$$Ph\cdot + PhCH_3 = PhH + PhCH_2\cdot$$

then

$$2PhCH_2 = (PhCH_2)_2$$

In the absence of toluene, benzophenone and fluorenone may be formed by reaction of phenyl and benzoyl radicals, which would suggest that the benzoyl radicals live long enough to react with the stationary

concentration of phenyl radicals. The increase in percentage decomposition when no toluene catcher is present suggests possible involvement of the parent molecule in some type of chain mechanism.

e.g. $Ph\cdot + PhCOOCOPh = $  $+ PhCO\cdot + H_2$

$PhCO\cdot = Ph\cdot + CO$ etc.

or $Ph\cdot + PhCOOCOPh = PhCOPh + PhCO\cdot$

and $PhCO\cdot = Ph\cdot + CO$, etc.

Whatever the complicating reaction, it can apparently be removed by the addition of workable amounts of toluene and for subsequent experiments, this addition was made.

Mass spectrometric examination of the toluene from an experiment showed a strong 78^+ peak indicating that benzene is a product. This supports the occurrence of the reaction

$$Ph\cdot + PhCH_3 \longrightarrow PhH + PhCH_2\cdot$$

Effect of variation of benzil partial pressure.

It should be possible to determine whether the decomposition was first order with respect to benzil or not, by varying the partial pressure of benzil and measuring the rate of production of carbon monoxide at each value. Such experiments were performed and the non-appearance of the spectrum of fluorenone on IR analysis of the products confirmed that a large enough excess of toluene was present.

The results are tabulated:

Benzil: Variation of Benzil Partial Pressure.

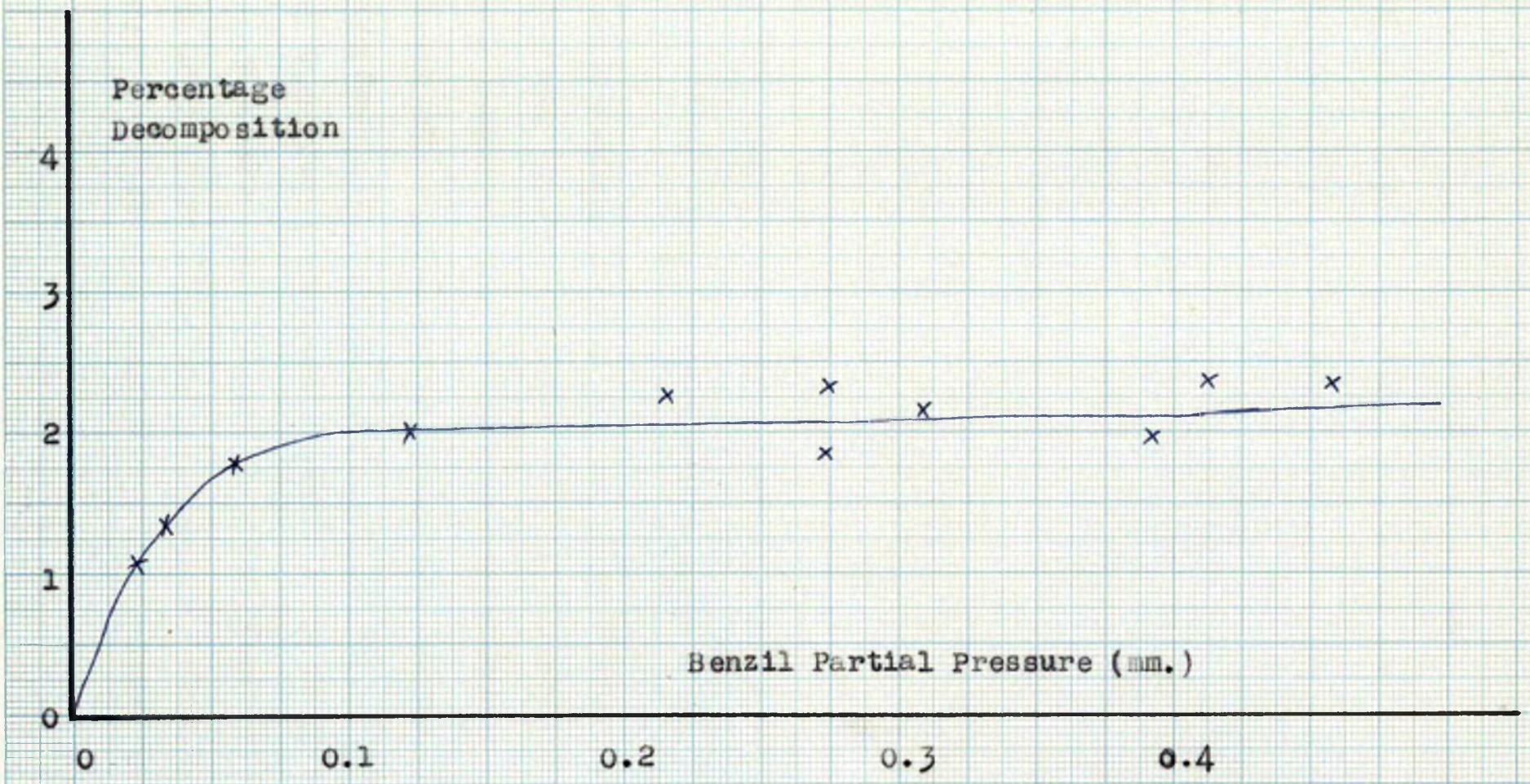


Fig.19.

TABLE 11

Expt.	Contact time (secs)	P_{bz} (mm)	$P_{tol.}$ (mm)	% decomposition.
36	0.56	0.025	1.02	1.11
37	0.57	0.036	1.08	1.45
38	0.55	0.060	0.96	1.81
39	0.55	0.124	2.15	2.01
40	0.55	0.218	2.30	2.52
41	0.55	0.276	1.79	2.37
42	0.55	0.275	1.97	1.86
43	0.55	0.31	2.27	2.21
44	0.55	0.396	1.91	1.99
45	0.55	0.415	1.92	2.58
46	0.55	0.46	1.91	2.37

(Above experiments at 540°C)

The plot of percentage decomposition against partial pressure of benzil (shown opposite) is roughly horizontal over a four times factor in partial pressure. It was not practicable, with the system used, to provide a sufficient excess of toluene for higher pressures of benzil. The fall-off in rate at very low partial pressures of benzil may be due to a first-second order transition if there are insufficient collisions to maintain the first order rate. Though the data are rather scattered, the horizontal nature of the plot suggests that the decomposition is first order with respect to benzil in

certain regions of concentration.

Variation of the contact time.

Glazebrook and Pearson photolysed acetophenone at temperatures below 150°C; and noted that benzil was amongst the products. At such low temperatures the benzoyl radical is apparently stable enough to be the reaction intermediate. It seemed possible that benzoyl radicals would have a long enough life to collide and recombine even at 540°C, since the recombination presumably has zero, or a low, energy of activation.

If recombination did occur, the extent of the decomposition to carbon monoxide would be expected to be progressively retarded as the benzoyl radical concentration increased. Increase in contact time would cause increased decomposition and a plot of percentage conversion against contact time should indicate wether recombination occurs. A series of experiments were performed at 539°C over which the contact time was varied.

TABLE 12

Expt.	contact time (secs)	P_{bz} (mm)	$P_{tol.}$ (mm)	% decomposition
47	0.535	0.125	1.90	0.96
48	1.32	0.130	2.18	2.18
49	1.54	0.108	2.14	2.77
50	2.68	0.05	2.02	4.62

Benzil: Variation of Contact Time.

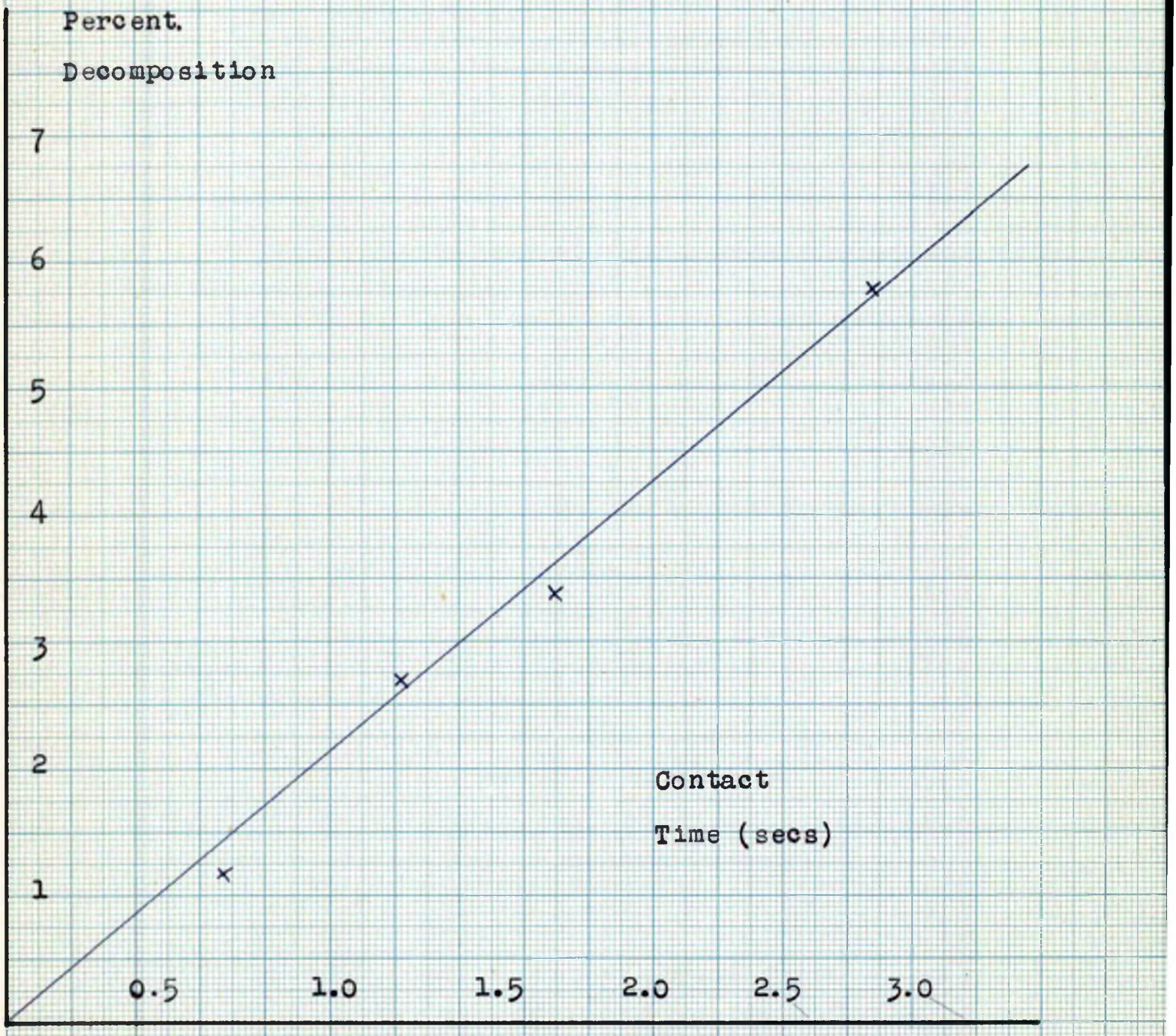


Fig.20.

TABLE 15

Expt.	contact time (secs)	P_{bs} (mm)	$P_{tol.}$ (mm)	% decomp$^{n.}$	log $\frac{100}{100-\%}$
51	0.40	0.37	1.29	15.0	0.0711
52	0.45	0.30	1.19	16.4	0.078
53	0.506	0.215	1.12	22.5	0.111
54	0.505	0.48	1.11	13.8	0.000
55	0.72	0.16	0.78	25.5	0.127
56	0.75	0.14	0.74	25.5	0.127
57	0.85	0.125	0.84	24.0	0.115
58	1.07	0.214	0.94	28.4	0.145
59	1.18	0.355	0.815	27.2	0.138
60	1.24	0.39	0.76	27.5	0.139
61	1.62	0.20	0.80	34.1	0.181
62	1.69	0.212	0.82	35.8	0.176
63	2.28	0.14	1.17	37.9	0.207
64	2.52	0.15	1.11	37.9	0.207

Benzil:

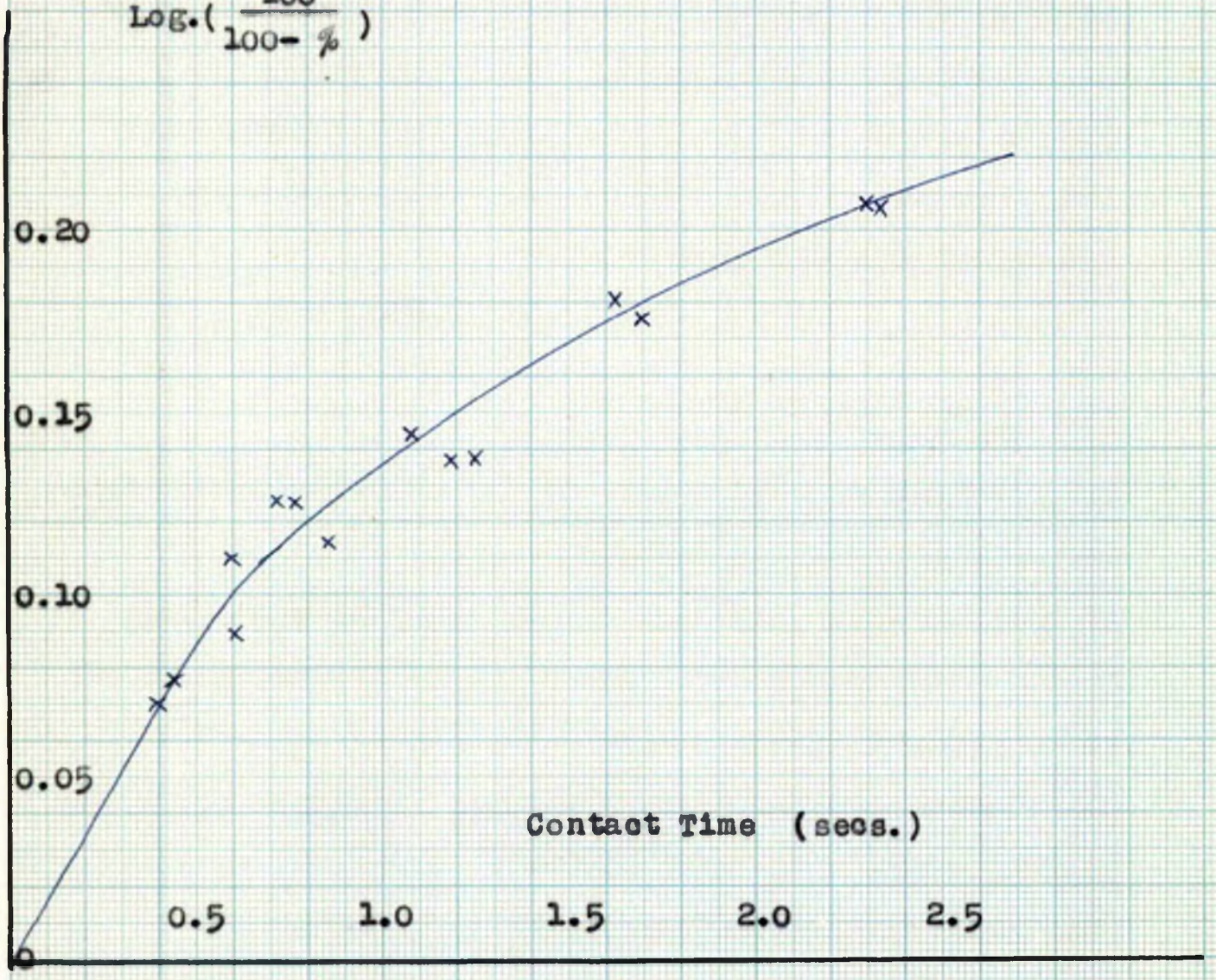


Fig.21.

The plot of percentage decomposition against contact time shown opposite is seen to be a straight line through the origin, which supports the view that benzoyl radicals under these conditions of low pressure and high temperature do not recombine.

Variation of contact time at high percentage decomposition.

Several experiments were performed at a higher temperature (597°C) to find whether the linear relationship between percentage decomposition and contact time still held. The results are tabulated opposite. The difficulty in maintaining a very steady partial pressure of benzil can be seen from these experiments performed on several consecutive days.

At such high conversions, it is more accurate to plot

$$\log_{10} \frac{100}{100 - \%\,\text{decomp.}^{n}}$$ against contact time.

This plot (shown opposite) is seen to fall off at high contact time. There could be several explanations for this:

(i) inefficiency of the liquid air trap before the cupric oxide furnace, at low contact time, allowing toluene to reach the furnace and be oxidised to carbon dioxide.

(ii) reaction between the benzoyl radicals and toluene, or any of the other radicals which might be present.

(iii) recombination of the benzoyl radicals to benzil.

(iv) inhibition of the benzoyl decomposition by the carbon monoxide formed.

(1) was tested for by carrying out a blank experiment with toluene alone, and no oxidation to carbon dioxide occurred.

The possibility of inhibition by the carbon monoxide produced was tested for by carrying out two pairs of experiments, at 538°C, one pair in argon carrier gas and the other with carbon monoxide as a carrier gas. The results are tabulated:

TABLE 14

Expt.	Contact time (secs)	P_{bs} (mm)	P_{tol} (mm)	Carrier gas	% decomp^{n}.	k_{uni} x 10
65	0.70	0.197	1.00	Ar	19.8	3.77
66	0.70	0.181	1.86	CO	20.8	3.17
67	0.70	0.41	1.89	Ar	19.9	3.88
68	0.70	0.50	1.41	CO	19.2	3.94

The carrier gas pressure used was 2 mm. mercury. The rates of decomposition for experiments in carbon monoxide carrier were not markedly lower than for those in argon, so carbon monoxide apparently exerts little inhibiting effect on the overall decomposition of benzil to carbon monoxide.

Until the infra-red spectrometer became available, there was no method of testing whether the fall off in the plot of percentage decomposition against contact time at high conversion was due to the benzoyl radicals combining with themselves or with any other radicals which might have been present.

For the experiments for which the results appear in table 10 it was noted that a three times excess in partial pressure of toluene over benzil was required to achieve a steady extent of decomposition at about 10% conversion. For the experiments at higher conversion (table 13) the excess in partial pressure of toluene over benzil was about five times, but this may not have been sufficient to remove all the phenyl radicals and prevent their complicating the first order production of carbon monoxide.

Summary.

At low conversion (< 10%) the decomposition of benzil to carbon monoxide appeared to be first order with respect to benzil at partial pressures of benzil greater than 0.06 mm, and with a five times excess in partial pressure of toluene over benzil.

Under these conditions, the mechanism appeared to be

$$PhCOCOPh \rightarrow 2PhCO\cdot \rightarrow 2Ph\cdot + 2CO$$

and the reactions:

$$Ph\cdot + PhCCl_3 \rightarrow PhH + PhCCl_2\cdot$$

$$2PhCCl_2\cdot \rightarrow (PhCCl_2)_2$$

took place. At higher temperatures and conversions there appeared to be some complication causing a retardation of the decomposition to carbon monoxide.

If the above mechanism held, benzene and carbon monoxide should be formed in equal amounts, so an analysis of the amount of benzene

TABLE 15

Expt.	Temp. (°C)	Contact time (secs)	P_{bz} (mm)	P_{tol} (mm)	$\frac{C_6}{decomp}^n$.	$\log_{10}k_{uni}$	$10^3/T$ (°K)
69	666	0.497	0.075	0.90	66.7	0.352	1.065
70	666	0.490	0.091	0.98	61.0	0.285	1.065
71	641	0.525	0.037	1.0	55.6	0.187	1.094
72	659	0.55	0.076	0.94	50.9	0.126	1.096
73	625	0.486	0.093	0.58	58.6	0.005	1.116
74	624	0.56	0.15	0.82	58.4	$\bar{1}$.942	1.114
75	596	0.55	0.17	0.78	30.2	$\bar{1}$.614	1.151
76	597	0.56	0.14	0.80	25.0	$\bar{1}$.667	1.149
77	579	0.68	0.15	1.0	11.7	$\bar{1}$.261	1.174
78	579	0.58	0.14	0.86	12.0	$\bar{1}$.345	1.174
79	579	0.57	0.15	0.84	10.6	$\bar{1}$.292	1.174
80	558	0.55	0.14	0.90	4.86	$\bar{2}$.966	1.205
81	558	0.56	0.15	0.91	4.76	$\bar{2}$.959	1.205
82	558	0.55	0.16	0.90	5.02	$\bar{2}$.948	1.205

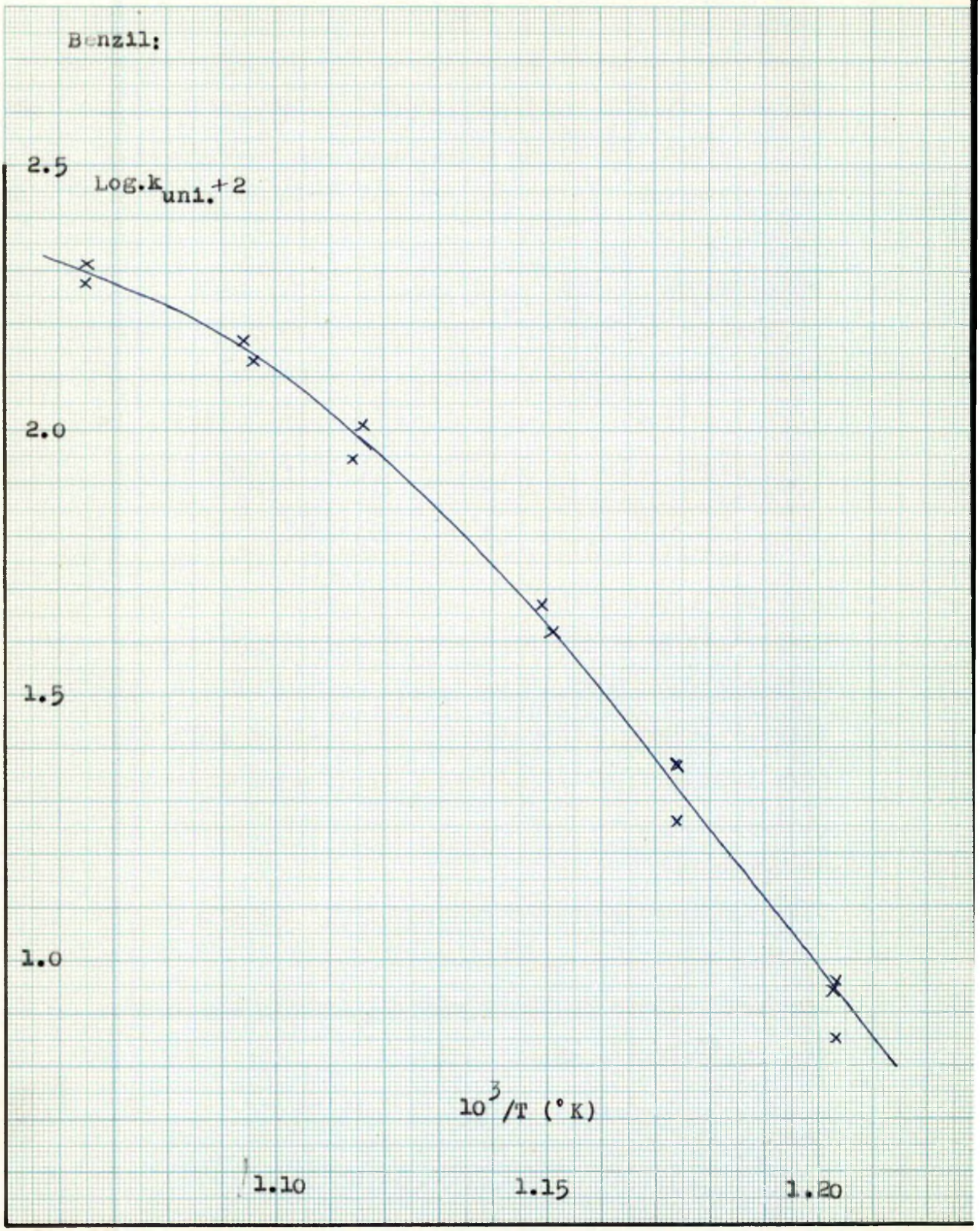


Fig. 22.

formed should be helpful in checking whether this mechanism was the true one. The mass spectrometer should be a suitable instrument for the benzene analysis and would also give some indication if aldehyde were present (e.g. from the reaction of benzoyl radicals with toluene).

Benzene analysis.

This was performed on the mass spectrometer by the peak ratio method.[60] Tests showed that with mixtures of benzene in toluene of about 10% composition, an analysis could be performed within about 5% inaccuracy. This should be sufficient to determine whether most of the phenyl radicals are caught as benzene or not.

A series of experiments were performed at varying temperatures with about a five times excess in partial pressure of toluene over benzil, and both the carbon monoxide and benzene were measured. The carbon monoxide figures for these experiments are shown in table 15 opposite, and a plot of $\log_{10} k_{uni}$ against $10^5/T$ (°K) (also shown opposite) is seen to fall off at higher temperatures, in agreement with the idea that some mechanism is retarding the decomposition.

The figures for the benzene analyses for some of these experiments are tabulated below:

(Standard: A 4% (by gm. wt.) mixture of benzene in toluene has a corrected 78/91 peak ratio of 5.97).

TABLE 16

Expt.	Temp. (°C)	Conv.[d] TS/BI ratio (%)	% benzene (by gc. wt.)	wt. toluene (gm)	moles benzene	moles CO	moles benzene / moles CO
69	666	14.5	9.60	0.75	9.0×10^{-4}	1.57×10^{-3}	0.575
71	641	6.25	4.18	0.74	4.0 "	9.10×10^{-4}	0.44
72	639	7.35	4.85	0.68	4.25 "	8.90	0.48
74	624	13.90	9.50	0.85	4.80 "	8.80	0.49
75	625	6.50	4.20	0.65	3.52 "	6.90	0.51
76	606	6.15	4.10	0.78	4.10 "	7.80	0.545
77	579	2.97	1.78	1.47	3.25 "	5.61	0.58
80	558	1.09	0.75	1.80	1.68 "	2.06	0.835

From the last column of figures, it can be seen that at lower temperatures (and lowest conversion) the ratio of moles benzene to moles carbon monoxide approaches progressively nearer to unity, (with the exception of the first result, which may be erroneous). Unfortunately, at low conversion, the analysis of a small yield of benzene in a relatively large amount of toluene cannot be carried out very accurately and it was not possible to pursue the benzene analysis to conditions of low percentage decomposition of benzil. However, the tendency of the benzene/carbon monoxide ratio to unity, supports the earlier indication that the benzil decomposition is first order at low percentage decomposition and takes place by the mechanism

$PhCOCOPh = 2PhCO- \xrightarrow{rapid} 2Ph- + 2CO$

followed by $Ph- + PhCH_3 = PhH + PhCH_2-$

For several experiments, a white solid distilled over from the decomposition products after the toluene. Its melting point was 49-51°C, which suggests dibenzyl (M.P. 51°C).

The fact that the (benzene / carbon monoxide) ratio was much less than unity at high conversion, where the amount of carbon monoxide was less than that expected on the reaction mechanism outlined, suggests that the phenyl radicals are in some way involved in the retardation of the overall decomposition, and that this is not simply due to the recombination of benzoyl radicals.

At high conversion, then, there appears to be loss of phenyl radicals. Several possible modes of loss could be postulated:

(a) Reaction of the radicals at the furnace wall, probably with deposition of carbon and production of hydrogen and other products.

(b) Dimerisation to diphenyl.

(c) Reaction with benzoyl radicals to give some involatile product e.g. benzophenone.

(d) Substitution into the benzil or toluene.

(a) To investigate the possibility of phenyl radicals decomposing at the wall, experiments were performed to measure the amount of carbon deposited in the furnace and the amount of hydrogen formed during an experiment. The carbon was measured by burning off in a stream of oxygen (with the furnace at 720°C) and measuring the

carbon dioxide produced.

TABLE 17

Expt.	Temp. (°C)	Contact time (secs)	P_{bz} (mm)	$P_{tol.}$ (mm)	moles CO	moles carbon deposited	moles benzene / moles CO
85	666	0.51	0.156	1.55	1.15×10^{-5}	5.20×10^{-4}	0.62
84	665	0.52	0.146	1.60	1.15 "	5.20 "	0.59

The figures for the (benzene / carbon monoxide) ratio are substantially less than unity, showing appreciable loss of phenyl, and the carbon dioxide figures indicate substantial deposition of carbon. Further experiments showed that the high yield of carbon dioxide was partly due to some of the toluene catcher and tap grease volatiles being oxidised in the furnace. A subsidiary liquid oxygen-cooled trap was fitted just before the furnace and the oxygen stream pressure kept below 10 mm to increase the freezing efficiency.

TABLE 18

Expt.	Temp. (°C)	Contact time (secs)	P_{bz} (mm)	P_{tol} (mm)	moles CO	moles C deposited
86	660	0.49	0.146	1.54	1.18×10^{-5}	8.40×10^{-6}
86	668	0.95	0.145	0.79	7.54×10^{-4}	1.14×10^{-4}

These results should give a true measurement of the amount of carbon deposited in the furnace. An increase in contact time and

drop in the toluene / benzil ratio is seen to give increased deposition of carbon. When a phenyl radical decomposes at the wall, we might expect the deposition of 1 - 6 carbon atoms. If we take the moles carbon monoxide as being roughly equivalent to the number of phenyl radicals initially produced we may note that from one in ten to one in sixty phenyl radicals react at the wall under the conditions of experiments 85 and 86. At these high temperatures, this extent of phenyl escape does not seem unreasonable.

(b) Analysis of hydrogen and other products in the carrier gas stream.

Decomposition of phenyl radicals at the furnace walls might be expected to give hydrogen. This could normally be oxidised to water in the cupric oxide furnace, so the oxidant was replaced by iodine pentoxide. Hydrogen was circulated over this oxidant at 200°C, and mass spectrometric observation of the H_2^+ peak showed that the hydrogen was not oxidised. The reaction with carbon monoxide proved to be very slow, so subsidiary flasks were fitted to the apparatus to increase its volume and reduce the alteration in contact time due to the build-up of carbon monoxide. A scan of the carrier gas before and after an experiment showed that the gaseous products were hydrogen and methane.

Two separate experiments were performed, with analysis of benzene, methane and hydrogen.

TABLE 19

Expt.	Temp. (°C)	Contact time (secs)	p_{bz} (mm)	p_{tol} (mm)	moles CO	moles H_2	moles CH_4	moles benzene / moles CO
87	669	0.52	0.066	1.80	5.47×10^{-5}	1.06×10^{-4}	1.0×10^{-5}	-
88	664	0.56	0.076	1.60	5.08×10^{-5}	1.55×10^{-4}	1.50×10^{-5}	0.595
89	664	0.61	-	2.20	-	-	-	-

A blank experiment (89) with toluene alone, produced effectively no hydrogen, methane or benzene. All the hydrogen and methane produced in experiments 87 and 88 then, are due to the benzil decomposition in the presence of toluene. The relatively small amount of hydrogen (to carbon monoxide) confirms the indication of the earlier carbon figures that not many of the phenyl radicals react at the wall, yet the low benzene / carbon monoxide ratio indicates that the phenyl radicals are still not all being caught by the toluene.

The other three suggested modes of loss of phenyl were:

(b) dimerisation

(c) reaction with other radicals present e.g. benzyl

(d) substitution in toluene or benzene.

The infra-red spectrometer was not at this time available, and investigations were carried out on the involatile products using the mass spectrometer.

For all the experiments so far, the products trap coolant was carbice at -80°C, so carbon monoxide, hydrogen and methane remained

in the carrier gas as the first fraction of the products. After an experiment the toluene and other products of similar volatility, constituting the second fraction, were distilled into a tube over liquid oxygen from the products traps at room temperature; the remainder was the third fraction of the products.

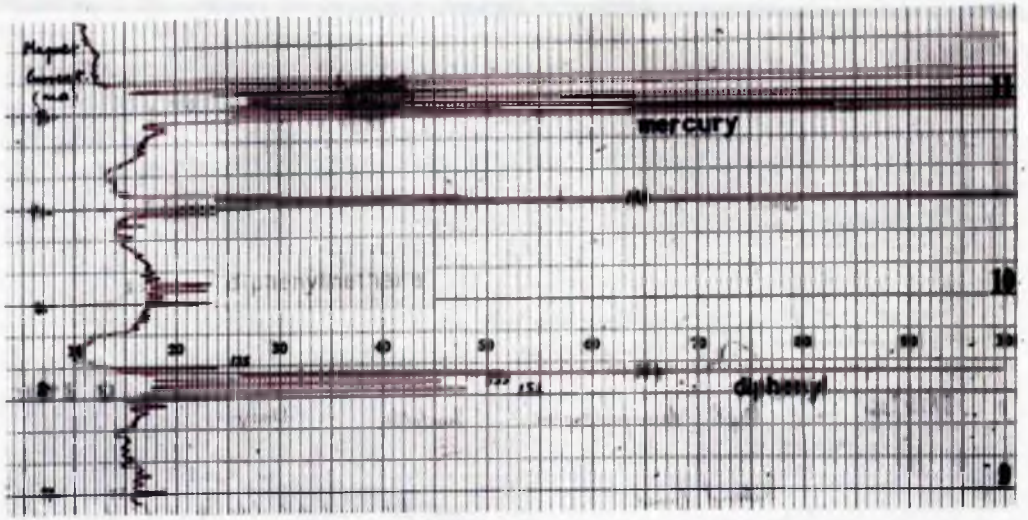
Second fraction.

This was analysed on the mass spectrometer, using a microburette for injection, and found to consist of a small amount of benzene in toluene. There was no 29^+ peak characteristic of the CHO group, but a standard scan with pure benzaldehyde showed no strong peak at 29^+, so this did not prove the absence of benzaldehyde as a product. (later infra-red analysis did prove this).

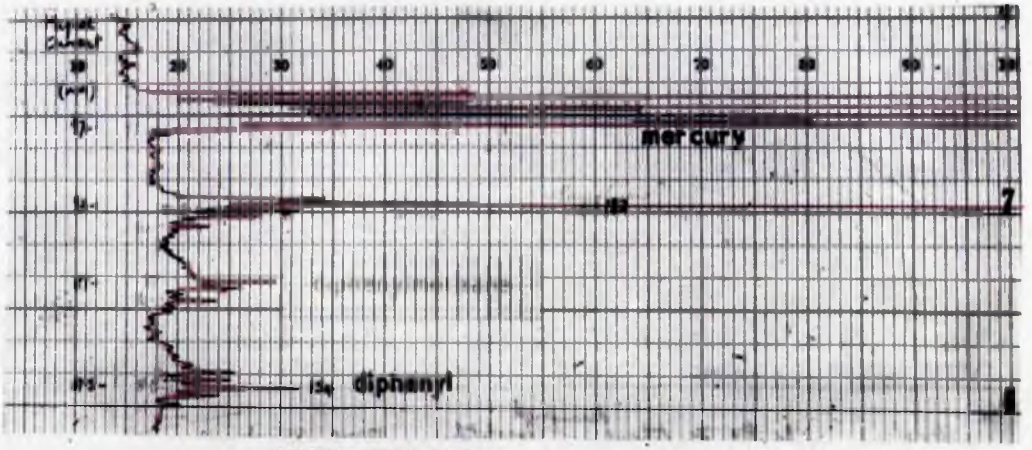
Third fraction.

For this involatile fraction, the mass spectrometer tube and head were heated, and the solid sample (after out-gassing) was injected through a bellows-type valve into a heated (100°C) flask over the mass-spectrometer leak.

Benzil itself gives no parent peak, but only a peak at mass 182^+, and peaks characteristic of the benzoyl (105^+) and phenyl (77^+) radical ions. Similarly, desoxybenzoin shows no parent, but only peaks characteristic of the benzyl, benzoyl and phenyl radical ions. Hence the mass spectrometer is no use for detecting benzophenone in benzil, or desoxybenzoin in a benzil-dibenzyl mixture, since the benzophenone and desoxybenzoin would have no distinct peaks.



WITHOUT TOLUENE



WITH TOLUENE

Fig. 23.

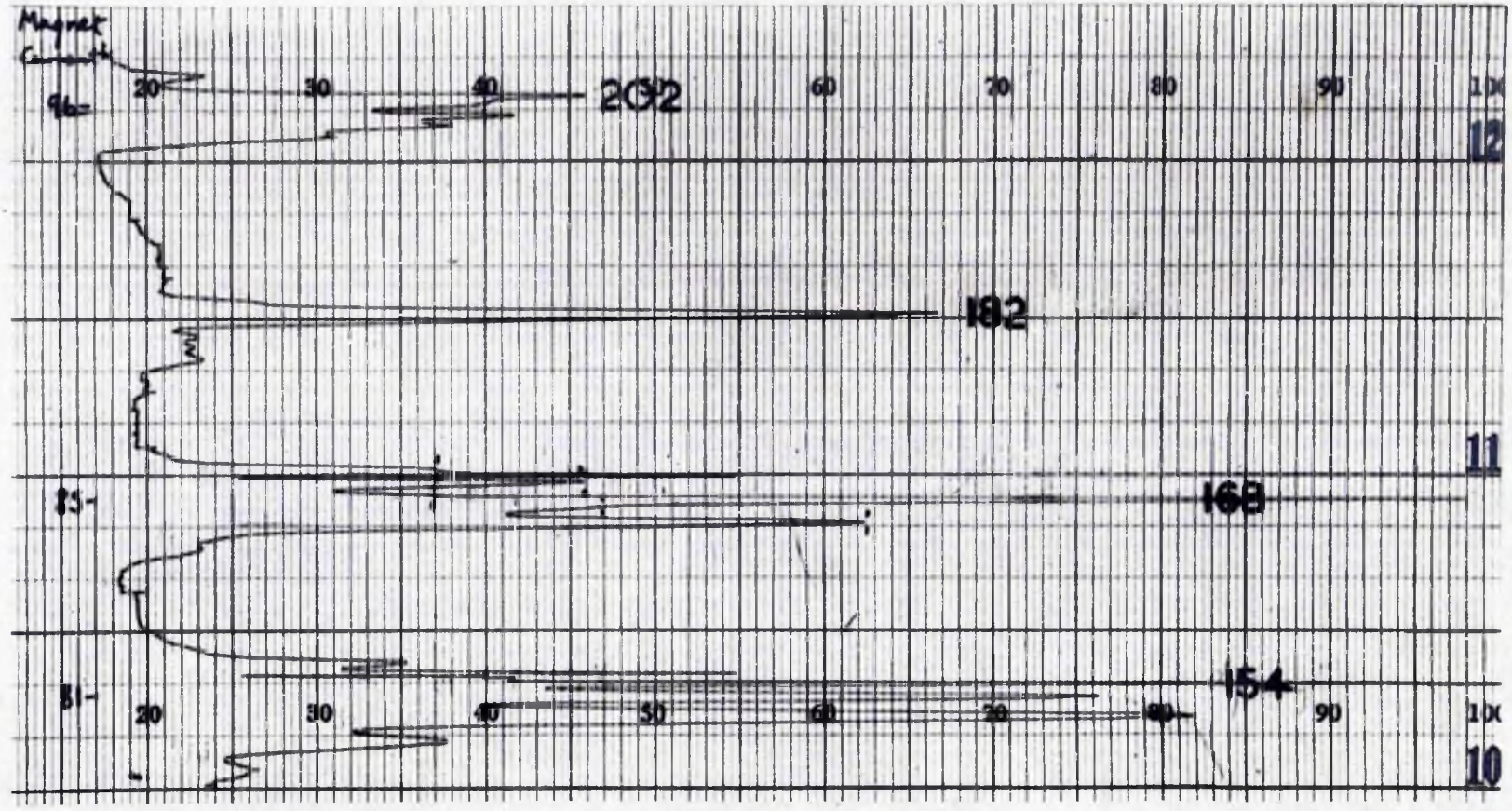

Magnet
Current
96-
85-
81-
20
30
40
50
60
70
80
90
100
202
182
168
154
12
11
10

Fig. 24.

Examination of the products of experiments with benzil without toluene catcher showed diphenyl as a product. Under these conditions, phenyl radicals evidently do recombine. The products of experiments with benzil and toluene catcher present at low conversion showed little trace of diphenyl. (The scans are shown opposite). This supports the initial assumption that phenyl radicals are removed by toluene under the experimental conditions.

Peaks for either diphenylmethane or one of the methyl diphenyls were found in this fraction, as is shown on the scan opposite of the products of experiment 87. This suggests that the phenyl radicals react by substitution as well as by hydrogen extraction with the toluene,

$$Ph\cdot + PhCH_3 = (PhCH_2.Ph) + H \quad \ldots(1)$$

$$\text{or } CH_3.C_6H_4.Ph. \text{ etc.}$$

$$\text{and} \quad Ph\cdot + PhCH_3 = PhH + PhCH_2\cdot \quad \ldots(2)$$

and explains why, even at low conversion, an equivalent amount of benzene to carbon monoxide was never found. The occurrence of diphenyl peaks in this scan suggests that the excess of toluene was not sufficient to catch all the phenyl radicals. The benzyl peak supports the occurrence of reaction (2).

Thus the mass spectrometer revealed a mechanism which could explain the "low" benzene analyses, but was not useful in detecting carbonyl containing products which might be formed to cause the fall-off in rate at higher conversion.

Reference scans of Experimental Products.

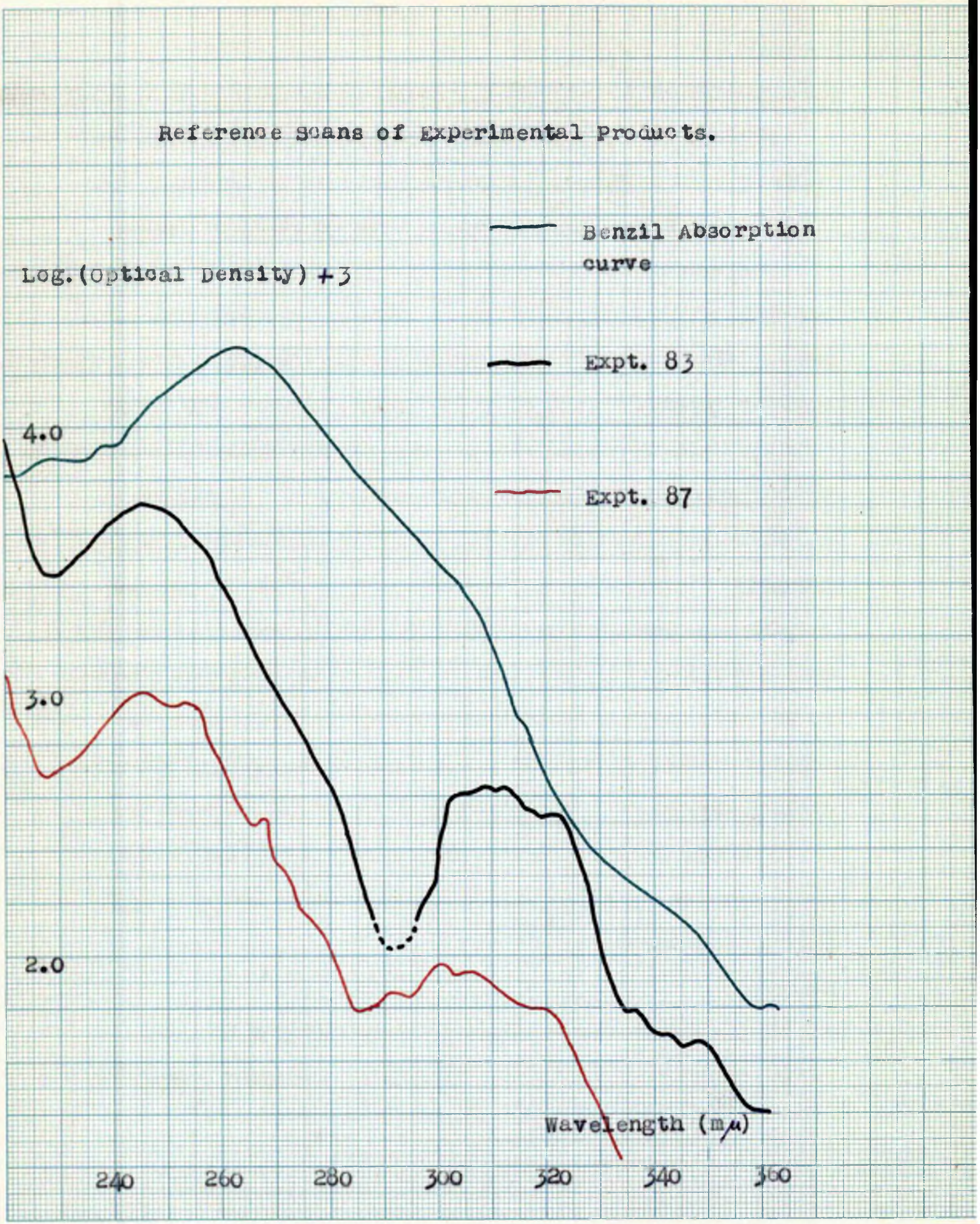


Fig. 25.

U.V. analysis of the involatile products of experiments at high conversion

Attempts were made to examine the involatile products in the third fraction for carbonyl-containing products by reference U.V. analysis of the methanol solutions against solutions of benzil.

A direct U.V. scan of the products showed a peak in the plot of log OD against wavelength at 260 mμ, whereas the benzil peak is at 262 mμ When the benzil contribution was blanked out, a double peak curve was revealed, as shown on the scans opposite. The strong absorption peak of benzil at 262 mμ made the measurement of the strength of absorption in the relative scan inaccurate but the position of the peaks suggested they were from a product containing the carbonyl grouping. Investigation of the spectra of some of the possible products e.g. benzophenone, fluorenone, benzaldehyde, diphenyl showed that they all have a rather similar peak, so the dual peak structure in the products reference scan may well be due to a mixture of carbonyl containing products. The shape of the peaks at 300-320 mμ particularly, suggested a mixture of products with adjacent peaks.

Reference analysis of the products of an experiment at low conversion e.g. experiment 49, showed no evidence for peaks apart from those of benzil.

Summary.

At low conversion (<10%) with about a five times excess in partial pressure of toluene over benzil, the mechanism appeared to b e:

TABLE 20

Expt.	Temp. (°C)	Contact time (secs)	% decomposition	$\log_{10} k_{uni}$	$10^3/T$ (°K)
75	566	0.56	20.2	$\bar{1}.614$	1.151
76	567	0.56	25.0	$\bar{1}.667$	1.149
77	579	0.58	11.7	$\bar{1}.931$	1.174
78	579	0.57	13.0	$\bar{1}.945$	1.174
79	579	0.55	10.6	$\bar{1}.898$	1.174
80	558	0.55	4.86	$\bar{2}.955$	1.205
81	558	0.56	4.76	$\bar{2}.939$	1.205
82	558	0.55	5.08	$\bar{2}.949$	1.205
44	540	0.55	1.68	$\bar{2}.840$	1.250
45	540	0.55	1.99	$\bar{2}.899$	1.250
41	537	0.555	2.31	$\bar{2}.948$	1.255
89	540	0.58	2.01	$\bar{2}.906$	1.250
90	559	0.55	1.81	$\bar{2}.919$	1.252
91	520	0.58	0.748	$\bar{2}.156$	1.281
92	511	0.55	0.418	$\bar{3}.897$	1.276
93	494	0.61	0.196	$\bar{3}.808$	1.304
94	493	0.61	0.144	$\bar{3}.938$	1.314
95	492	0.54	0.139	$\bar{3}.917$	1.326
96	482	0.59	0.095	$\bar{3}.906$	1.328
97	468	0.62	0.078	$\bar{3}.101$	1.350
98	466	0.55	0.068	$\bar{3}.020$	1.355

$$PhCOCOPh \longrightarrow 2PhCO\cdot \xrightarrow{(rapid)} 2Ph\cdot + 2CO.$$

$$Ph\cdot + PhCH_3 \begin{cases} \longrightarrow PhH + PhCH_2\cdot \\ \longrightarrow H\cdot + (Ph.CH_2.Ph) \\ \qquad\qquad \text{and } CH_3.C_6H_4.Ph \text{ etc.} \end{cases}$$

$$2(PhCH_2\cdot) \longrightarrow (PhCH_2)_2$$

At higher conversion (>10%) with the same excess of toluene, some phenyl radicals are apparently not caught by the toluene, some dimerise, and some may react with the benzoyl radicals or the benzil in such a way as to give carbonyl-containing products and retard the overall decomposition of benzil to carbon monoxide.

Temperature coefficient determination.

For this, flow experiments were performed at varying temperatures with a benzil partial pressure of about 0.1 mm. and about a ten times excess in partial pressure of toluene over benzil. A unimolecular rate constant was calculated on the basis of two molecules of carbon monoxide per initial split. The results are tabulated opposite and a plot of the data appears on the following page.

The graph of $\log_{10}k_{uni}$ against $10^3/T$ (°K) was a straight line and assessment of the results by the method of least squares gave the experimental E as 62.1 k cal/mole and $\log_{10}A$ as 15.30 in the equation $k = A_\infty - E/RT$ for the first order production of carbon monoxide from benzil.

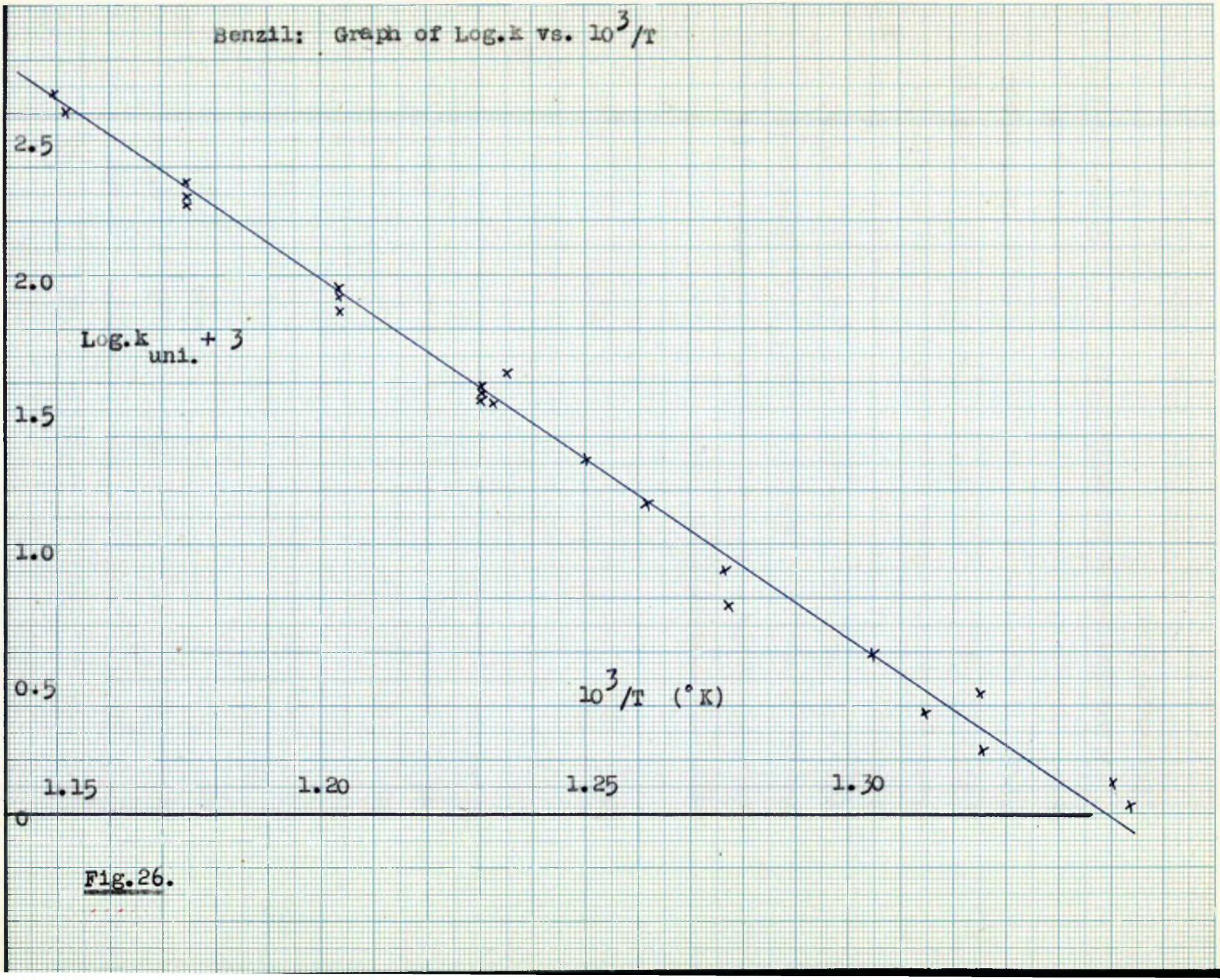

Benzil: Graph of Log.k vs. $10^3/T$
2.5
2.0
Log.$k_{uni.}$ + 3
1.5
1.0
0.5
$10^3/T$ (°K)
1.15
1.20
1.25
1.30
0

Fig.26.

Heterogeneity test.

As was mentioned in the introduction, a possible complication, even at these low partial pressures, is reaction of some of the radicals at the furnace wall. To check whether the decomposition of benzil was surface sensitive, arrangements were made to vary the surface / volume (S/V) ratio of the furnace. Pyrex is easier to work than silica and would stand temperatures up to half way up the experimental range without softening, so a furnace and concentric removable liners were constructed of pyrex. Experiments were performed under about the same conditions as the previous temperature coefficient experiments.

TABLE 21

Expt.	Temp. (^{o}C)	Contact time (secs)	S/V	$\log_{10}k_{uni}$	$10^{3}/T$ (^{o}K)
(a) both liners fitted					
99	476	0.39	6.66	$\bar{3}.060$	1.355
100	506	0.31	6.66	$\bar{3}.391$	1.299
101	527	0.426	6.66	$\bar{2}.166$	1.260
102	527	0.426	6.66	$\bar{2}.100$	1.260
(b) no liners.					
103	476	0.66	1.89	$\bar{3}.905$	1.352
104	500	0.65	1.89	$\bar{3}.560$	1.324
105	529	0.625	1.89	$\bar{2}.206$	1.287
106	529	0.595	1.89	$\bar{2}.351$	1.293

Benzil: Test for Surface Reaction.

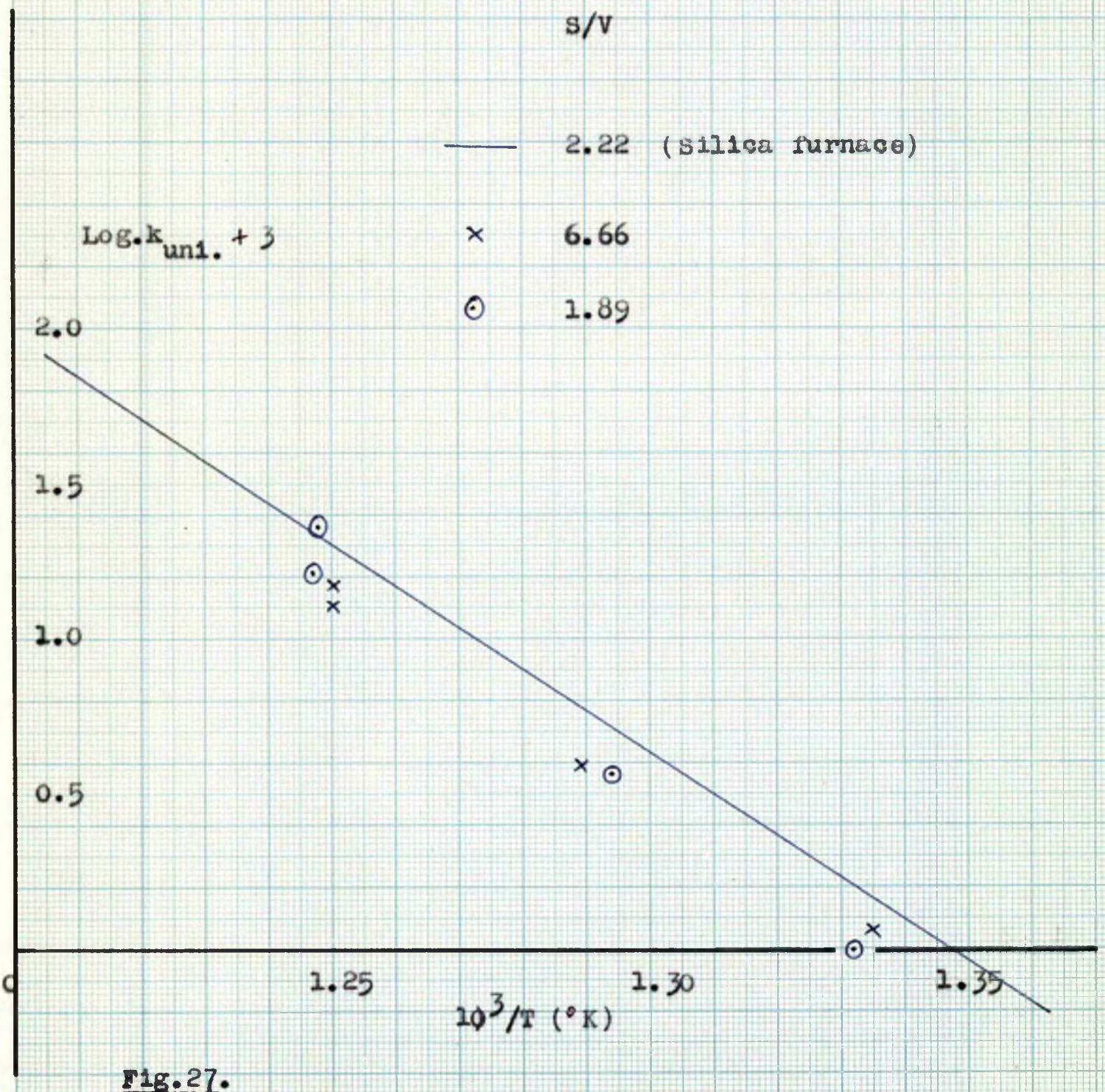


Fig.27.

APPARATUS FOR INTRODUCING TOLUENE TO REACTION VESSEL

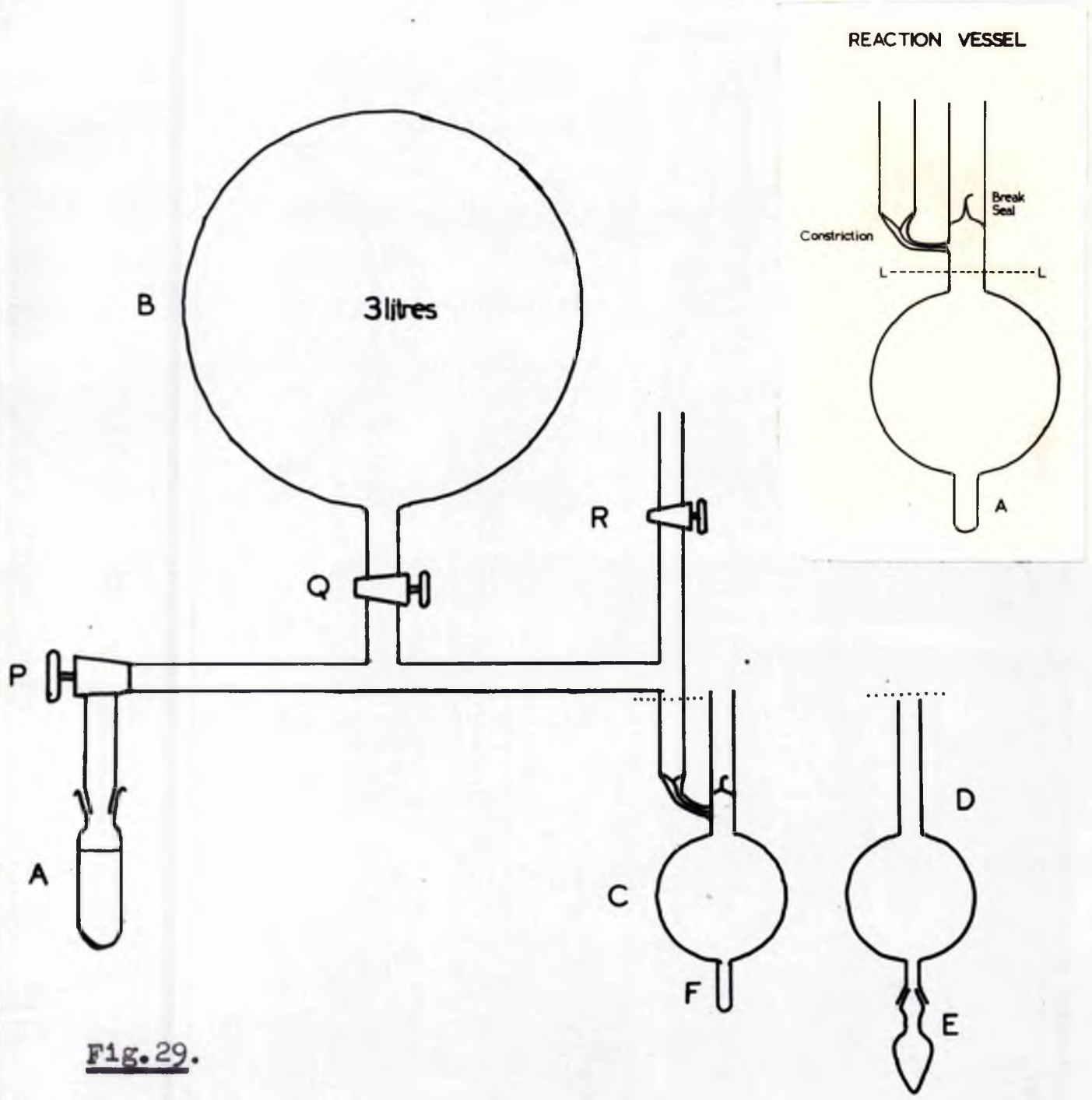


Fig.29.

The plots of $\log_{10} k_{uni}$ against $10^3/T$ (°K) for these experiments are parallel to, and quite close to the temperature coefficient plot for the silica furnace with no liners. (S/V = 2.22). Since a change in S/V ratio of more than three did not appreciably affect the rate of decomposition the reaction could be taken to be homogeneous. The discrepancy between the rates for the pyrex and silica furnaces may be due to error in estimation of the "hot length" of the furnaces. In plotting the temperature profile of the furnace, the estimation of the ends of the reaction zone is rather arbitrary, and the practice of taking the end of the reaction zone as that point where the temperature fell to 20 degrees below the average furnace temperature may have led to some error.

Reactions in a static system.

Though the temperature range covered by the "flow" experiments for the temperature coefficient determination was 150 degrees, it seemed possible that reactions carried out in a static system would allow the range to be extended lower by about a further 100 degrees.

Apparatus and experimental technique.

It was decided to heat benzil - toluene mixtures in 300 ml. pyrex bulbs, and analyse the carbon monoxide and other gaseous products on a modified form of the flow apparatus. Some means were required for introducing the reactants and excluding air. A diagram of the reaction bulb is shown opposite. Benzil was weighed in small tubes, introduced to the bulb, and the constriction was then sealed on at LL'.

A separate apparatus was required to introduce the toluene and its diagram is also shown opposite P75. The procedure for calibration was to first pump out this apparatus with the bulb D connected. The bulb B was allowed to fill with toluene vapour from container A immersed in a water bath at about two degrees below room temperature, tap P was closed, and the toluene frozen down into E, and weighed. Successive calibrations gave reproducible results within 5%, and the apparatus was calibrated for different toluene bath temperatures. Reaction vessels were sealed on to the apparatus as shown in the diagram, and a repeat of the calibration procedure introduced a known amount of air-free toluene into the apparatus. The reaction vessel was then sealed off at the constriction.

The furnace was constructed in a similar way to that for the flow experiments but with a wider bore, and its temperature was also controlled with a Sunvic-type furnace controller.

Before introduction to the furnace, the vessels were shaken thoroughly to encourage good mixing during reaction. Once in the furnace the vessels took about five minutes to warm up, and the reaction was taken as started when the temperature was within five degrees of that required.

Analysis of products.

The gaseous products were examined qualitatively by introduction of the mass spectrometer leak into the gas stream, and found to

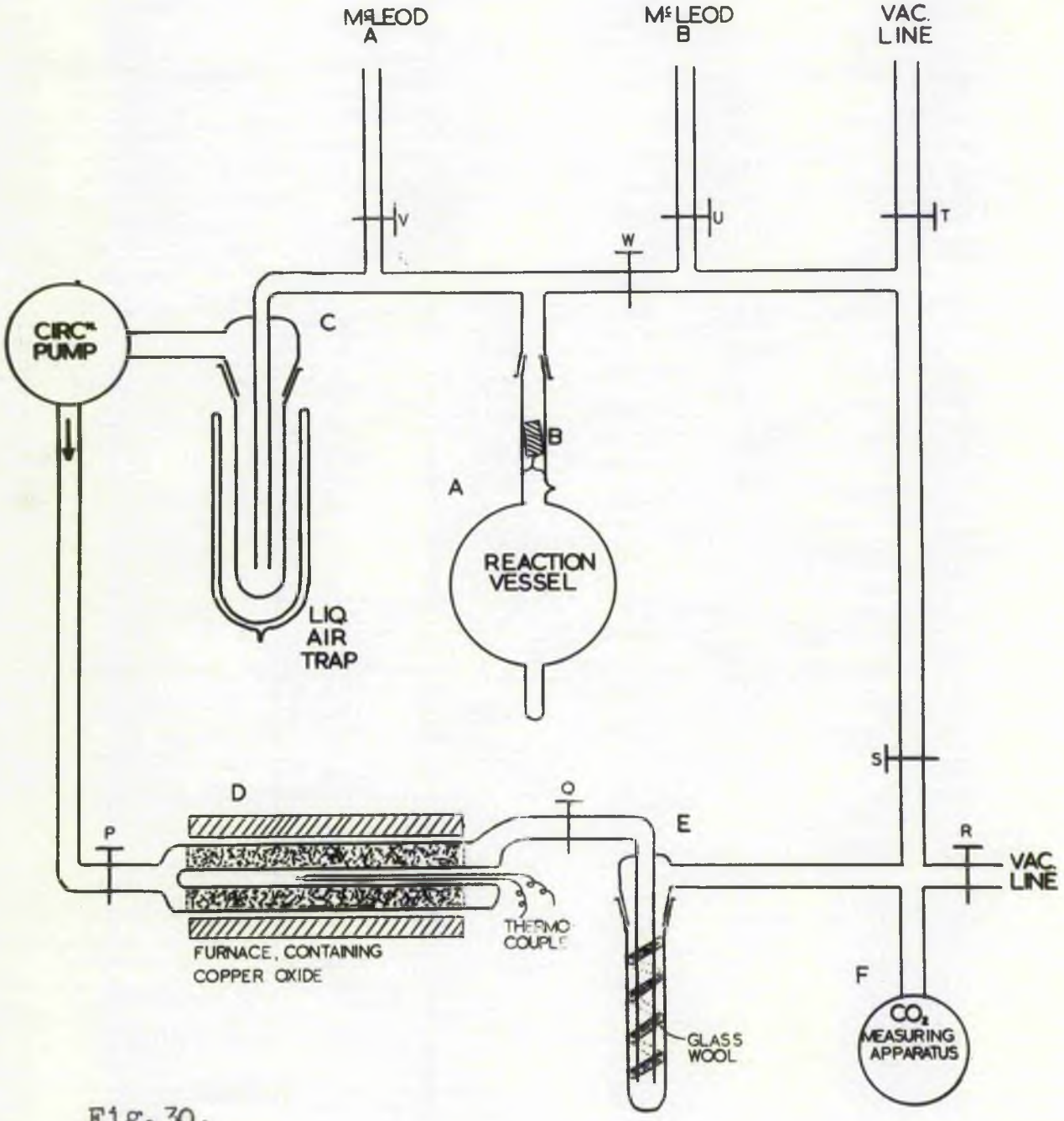

McLEOD A
McLEOD B
VAC. LINE
V
U
T
W
CIRC^N PUMP
C
B
A
REACTION VESSEL
LIQ. AIR TRAP
S
D
O
E
P
R
VAC. LINE
THERMO COUPLE
FURNACE, CONTAINING COPPER OXIDE
F
GLASS WOOL
CO2 MEASURING APPARATUS

Fig. 30.

consist mostly of carbon monoxide. The amount of carbon monoxide was measured quantitatively on an adaption of the flow apparatus, a diagram of which is shown opposite.

For this analysis the reaction vessel with products was fitted by a Quickfit cone to the apparatus, and had an iron core B. The apparatus was pumped out, and the circulation pump started. Liquid oxygen baths were placed round traps C and E, and tap F was closed. The break seal was destroyed with the core B and a magnet, and the toluene allowed to distil into trap C. The carbon monoxide was pumped out, as shown by the McLeod A, into the limb up to tap F. Argon was introduced into the line and the mixed gases circulated over the cupric oxide furnace. The carbon dioxide produced froze down in trap E and was measured as for the flow experiments.

The toluene was examined separately in the mass spectrometer, and contained some benzene, which was too small in amount to measure accurately. U.V. examination of the toluene fraction showed no peak for benzaldehyde.

A blank experiment with toluene alone gave very little gaseous product, and a small correction was applied for this.

The same techniques for analysis as for the flow experiments were applied to the products of the static experiments.

Three experiments were performed:

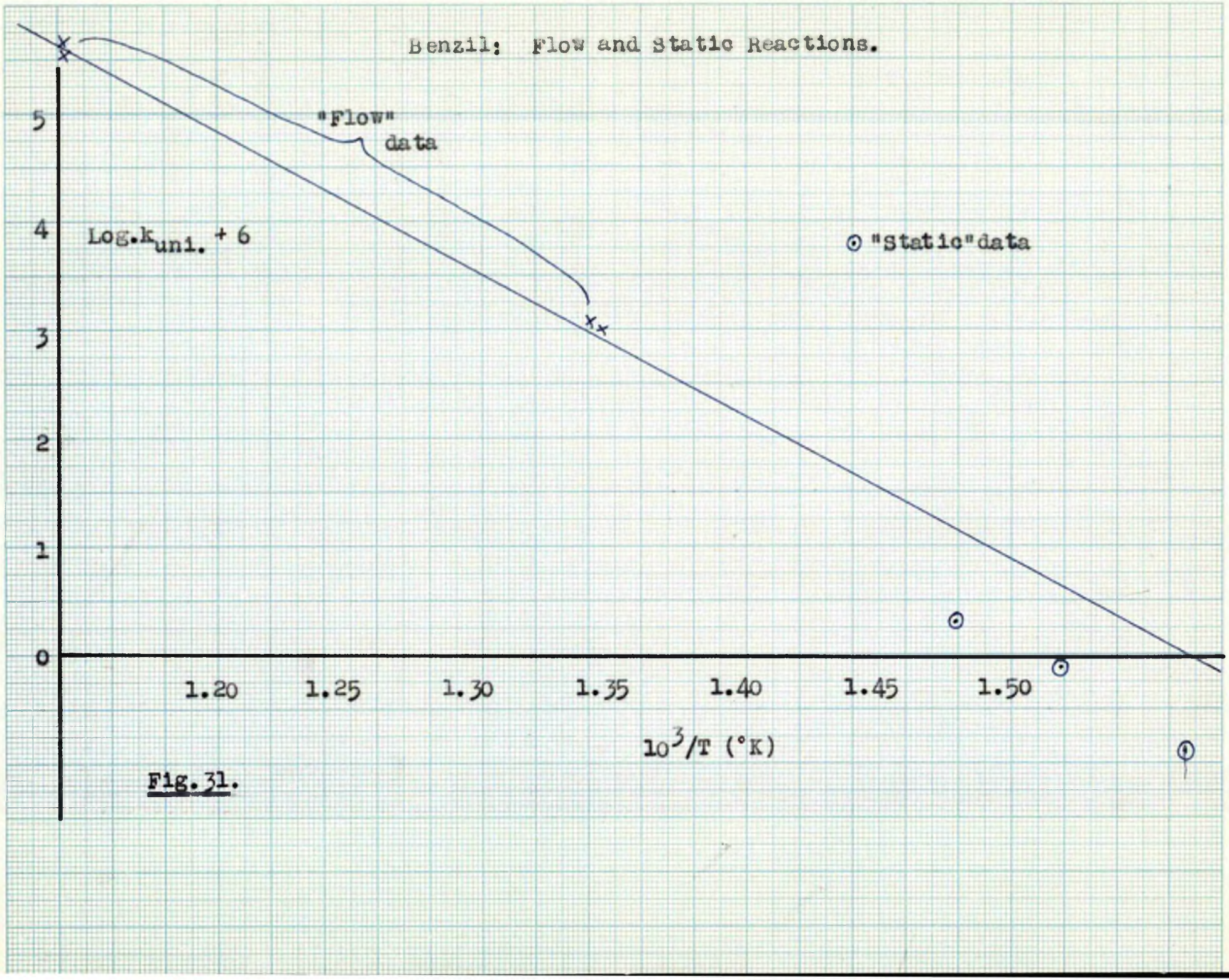

Benzil: Flow and Static Reactions.
"Flow" data
Log.k uni. + 6
"Static" data
5
4
3
2
1
0
1.20
1.25
1.30
1.35
1.40
1.45
1.50
10³/T (°K)

Fig.31.

TABLE 22

Expt.	Temp. (°C)	Contact time (secs)	P_{bz} (mm)	P_{tol} (mm)	$\log_{10} k_{uni}$	$10^5/T$ (°K)
107	404	215	55.5	396	$\bar{6}.512$	1.477
108	382	180	54.5	402	$\bar{7}.955$	1.527
109	382	300	55.5	402	$\bar{7}.118$	1.575

When these data are plotted on the same graph as the temperature coefficient for the flow experiments, the points are seen to lie well below the "flow" line, as is shown on the graph opposite. The points are about a factor of ten low in rate of decomposition to carbon monoxide. A factor as large as this would not be expected to be due to experimental error, and the fact that all three experiments are "low" by the same amount suggests some real reason and not experimental scatter.

Under flow conditions at low conversion, the linear plot of per cent. decomposition against contact time suggested that recombination of benzoyl radicals did not occur. Although the activation energy for recombination is presumably small, due to their instability at higher temperatures the concentration of benzoyl radicals even at high conversion is probably small, and the chance of mutual collision of benzoyl radicals slight. Phenyl radicals, however, might be expected to have a longer life under the flow conditions and could quite possibly pick up benzoyl radicals to give

carbonyl-containing products.

For the static experiments, the temperature was lower, and the benzoyl radical would be expected to be more stable and to have a longer life. Also, the partial pressures are very much higher and the chance of two benzoyl radicals colliding before they decompose is much higher than under the flow conditions. Also, there should be a good chance for benzoyl and phenyl radicals to react since the energy of activation for this reaction is presumably much smaller than for the phenyl attack on toluene.

Several experiments in the static system were carried out with benzil and toluene at higher temperatures, the toluene distilled away, and the involatile products inspected by reference U.V. analysis.

TABLE 23

Expt.	P_{bz} (mm)	P_{tol} (mm)	% decomposition
110	141	535	38.9
111	15.2	570	65.9
112	7.30	505	79.8
113	5.08	417	86.9
114	73	482	86.1
115	35.3	475	87.0
116	3.15	387	78.2
117	3.15	405	87.7

(All at 460°C for 180 mins).

Ultra-Violet Reference Peaks for the Involatile Products of Static Experiments.

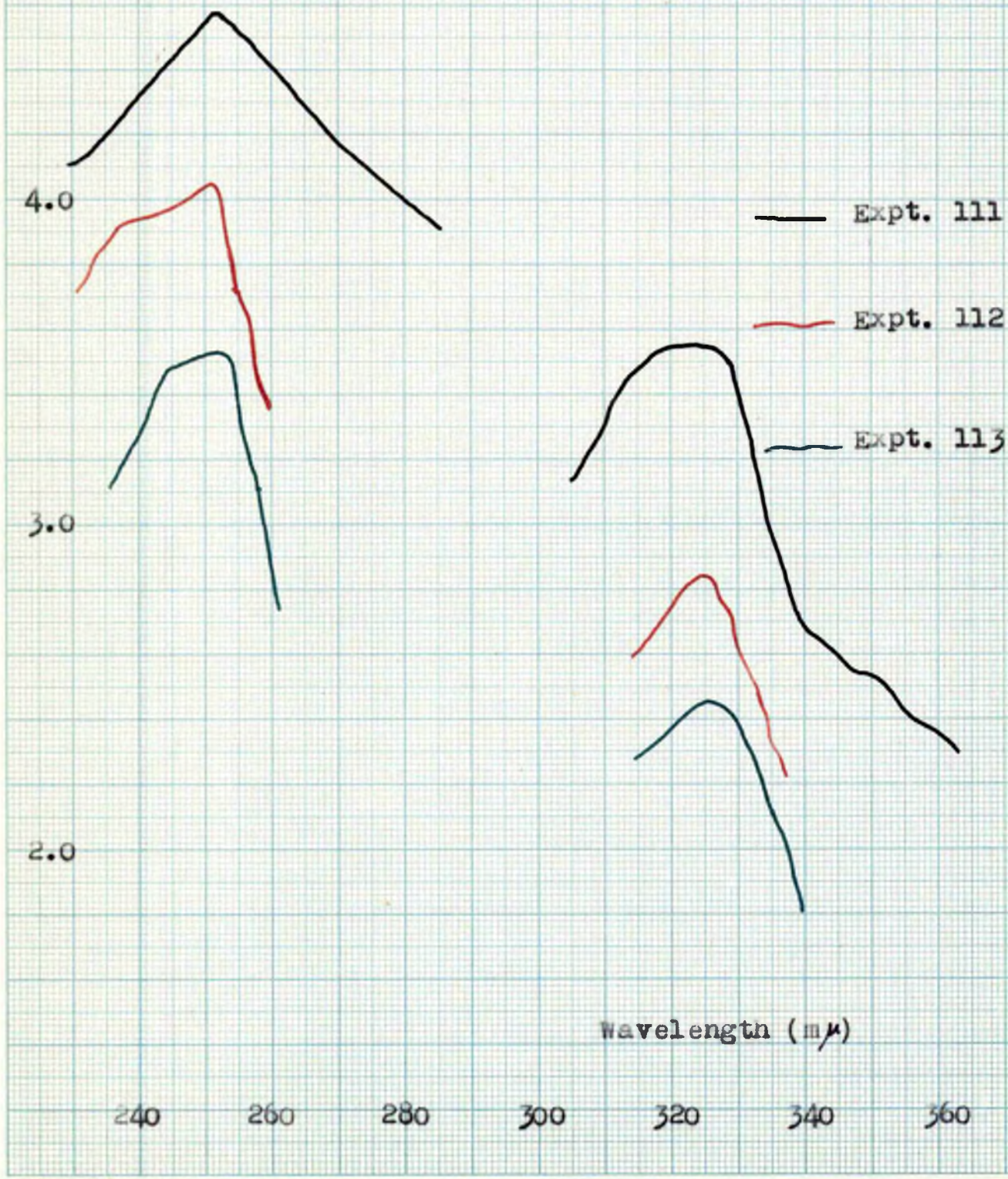


Fig. 32.

Ultra-Violet Reference Scans of the Involatile Products of Flow and Static Experiments at Low Conversion.

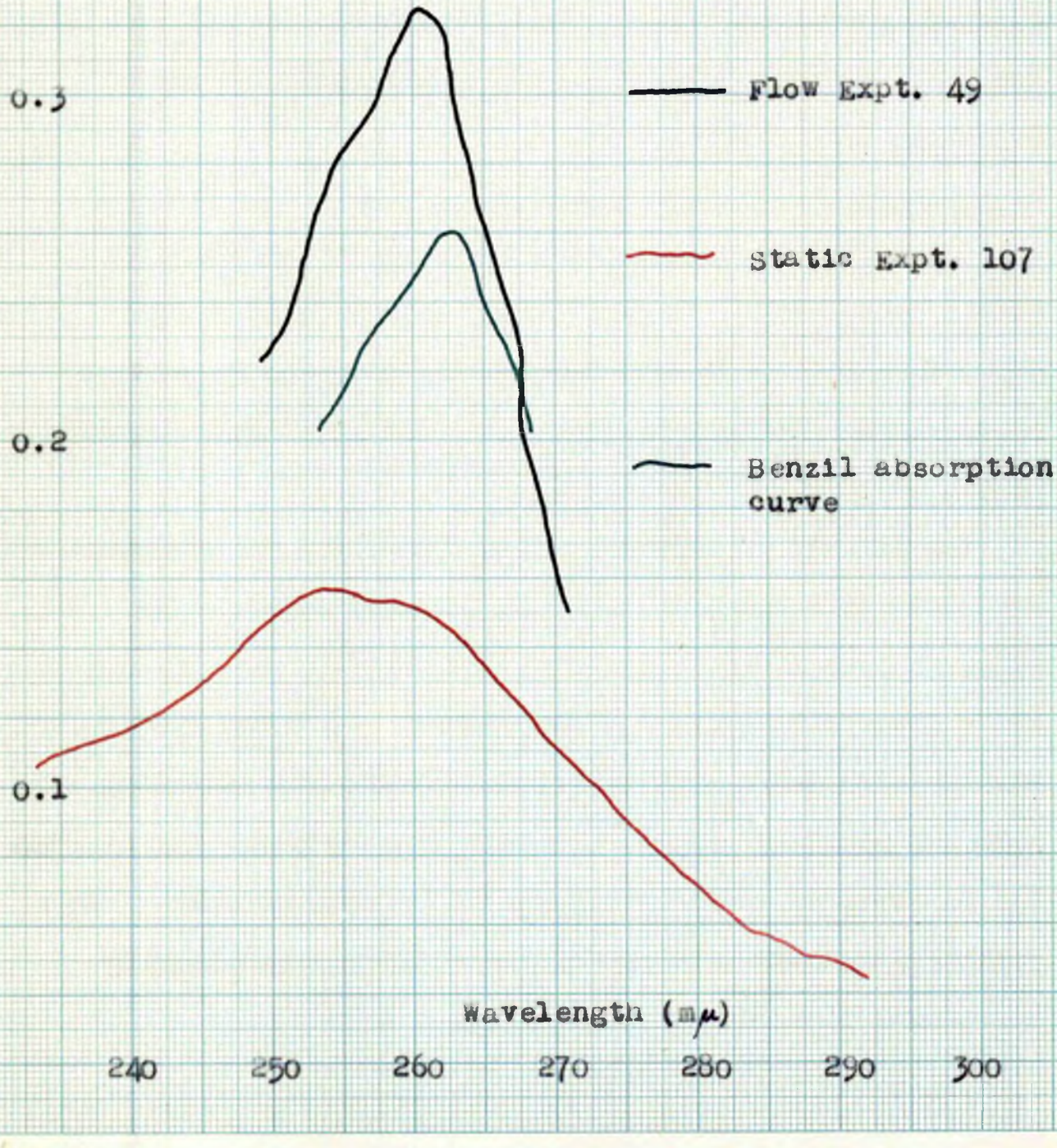


Fig. 33.

The rate equation from the flow data is $k = 10^{15.5} e^{-62100/RT}$ and using this expression to calculate the expected extent of decomposition after three hours treatment at 400°C this would be very close to 100%. The experimental figures are lower, which suggests that some mechanism for removing carbon monoxide from the system is operating. If this mechanism were only recombination of benzoyl radicals, more recombination, relatively, might be expected at higher partial pressures of benzil, but systematic variation of the benzil partial pressure gave only scattered results for the percentage decomposition.

U.V. analysis of the involatile products.

The direct U.V. spectrum of the products of experiment 114 shows a peak at 250 mμ whereas the peak for benzil is at 302 mμ U.V. reference scans against solutions of benzil for the products of experiments 111, 112, and 115 show a spectrum with double peaks at 252, 296 mμ.

The U.V. spectra of benzophenone; fluorenone; and deoxybenzoin are all rather similar and fall roughly in this region. The reference scans of the products are shown opposite and a comparison of the direct U.V. spectrum of the products of a static (107) and a flow (40) experiment, both carried to about the same conversion, shows the relatively greater peak shift from the benzil peak position for the static run products than for the flow run products. This presumably indicates a greater amount of carbonyl-containing by-

product under the static conditions.

Infra-red analysis.

The position and intensity of the carbonyl band in the infra-red spectra of aldehydes and ketones is closely governed by the environment of the carbonyl group so that it is often possible to determine from the band frequency, the type of structure in which the carbonyl group occurs. When an infra-red spectrometer became available, the products from static experiment 114 were inspected in the carbonyl band region. By comparison with standard scans it was seen that as well as excess benzil,[64] benzophenone[65] and fluorenone[66] were present, confirming suspicions aroused by the reference U.V. analyses. The benzophenone carbonyl peak was rather close to that for benzil but a reference technique of inspecting the solution against reference solution of benzil showed the benzophenone carbonyl band clearly. The benzophenone and fluorenone may be the products of the reaction of phenyl and benzoyl radicals. In view of the calculation made on the previous page on the extent of decomposition expected in the static experiments, the occurrence of excess benzil in the products indicates that benzoyl recombination probably occurs under these conditions.

As mentioned in the early part of this section, infra-red examination of the products of flow experiments confirmed that, for high conversion, benzophenone and fluorenone were present, but in relatively small amount. At low conversion these substances were

not detectable by infra-red.

SUMMARY.

Investigations of the involatile products of static reactions by a reference U.V. technique, and by infra-red direct and reference analysis showed the presence of carbonyl containing products. The presence of these products in uncertain amount removed the possibility of making any kinetic suppositions from the measurements of free carbon monoxide produced.

The Thermal decomposition of desoxybenzoin.

As mentioned in the introduction, work on desoxybenzoin would be expected to provide a link between the results on benzil and the earlier work on dibenzyl. In particular, if the bond dissociation energy for the central C-C bond of desoxybenzoin could be determined, and if the heat of formation of desoxybenzoin were known, it should be possible to calculate the heat of formation of the benzil radical. This would be an independent determination of this quantity, and its comparison with values from other sources would be interesting.

The apparatus and experimental technique used were exactly the same as for the flow experiments on benzil.

The effect of toluene.

First of all, experiments were performed to find the effect of toluene on the decomposition by varying the toluene partial pressure at 601°C.

TABLE 24

Expt.	Contact time (secs)	$P_{desoxybenzoin}$ (mm)	P_{tol}/P_{des}	P_{tol} (mm)	% decomposition
118	0.40	0.137	0	0	4.18
119	0.40	0.318	0.87	0.276	4.10
120	0.40	0.127	0.397	0.505	4.58
121	0.40	0.144	4.78	0.690	4.10

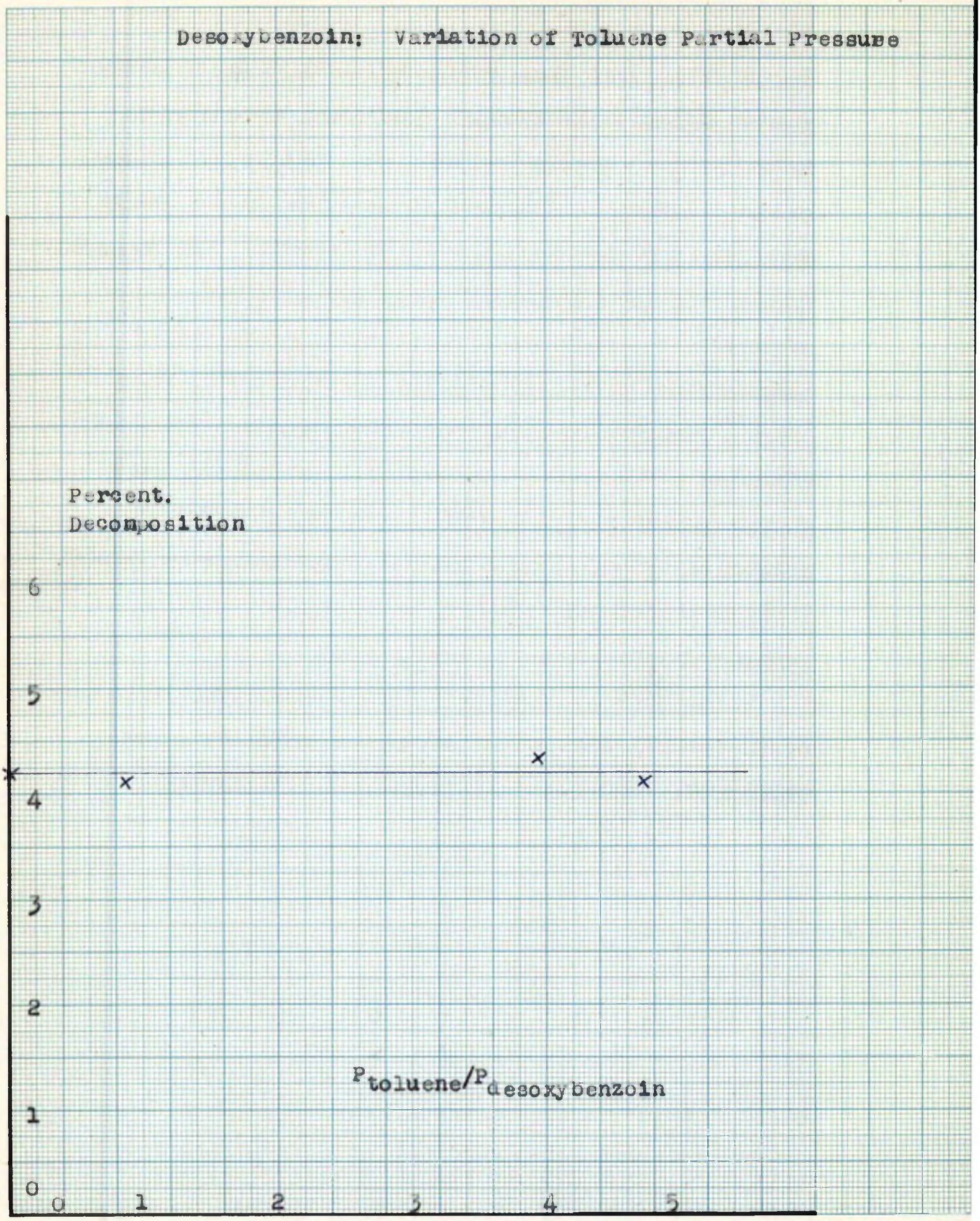

Desoxybenzoin: Variation of Toluene Partial Pressure
Percent.
Decomposition
6
5
4
3
2
1
0
0
1
2
3
4
5
$P_{toluene}/P_{desoxybenzoin}$

Fig. 34.

The plot of per cent. decomposition against the ratio of partial pressure toluene to deoxybenzoin (ptol/pdox), shown opposite is seen to be a horizontal straight line. Thus toluene appears to have no effect, at this extent of conversion, on the overall decomposition of deoxybenzoin to carbon monoxide. This suggested that, at this low conversion, there are not sufficient reactions of phenyl and benzoyl radicals to effect the overall rate of decomposition to carbon monoxide, and that there are no carbon monoxide producing chains, as suspected for benzil. Infra-red inspection of the involatile products confirms that some benzophenone is formed when toluene is not present, as toluene was injected for subsequent experiments to prevent this, particularly at higher conversion.

Variation of deoxybenzoin partial pressure.

To find whether the decomposition was first order with respect to deoxybenzoin, its partial pressure was varied over several experiments, other factors being kept reasonably constant.

Desoxybenzoin: Variation of Desoxybenzoin Partial Pressure.

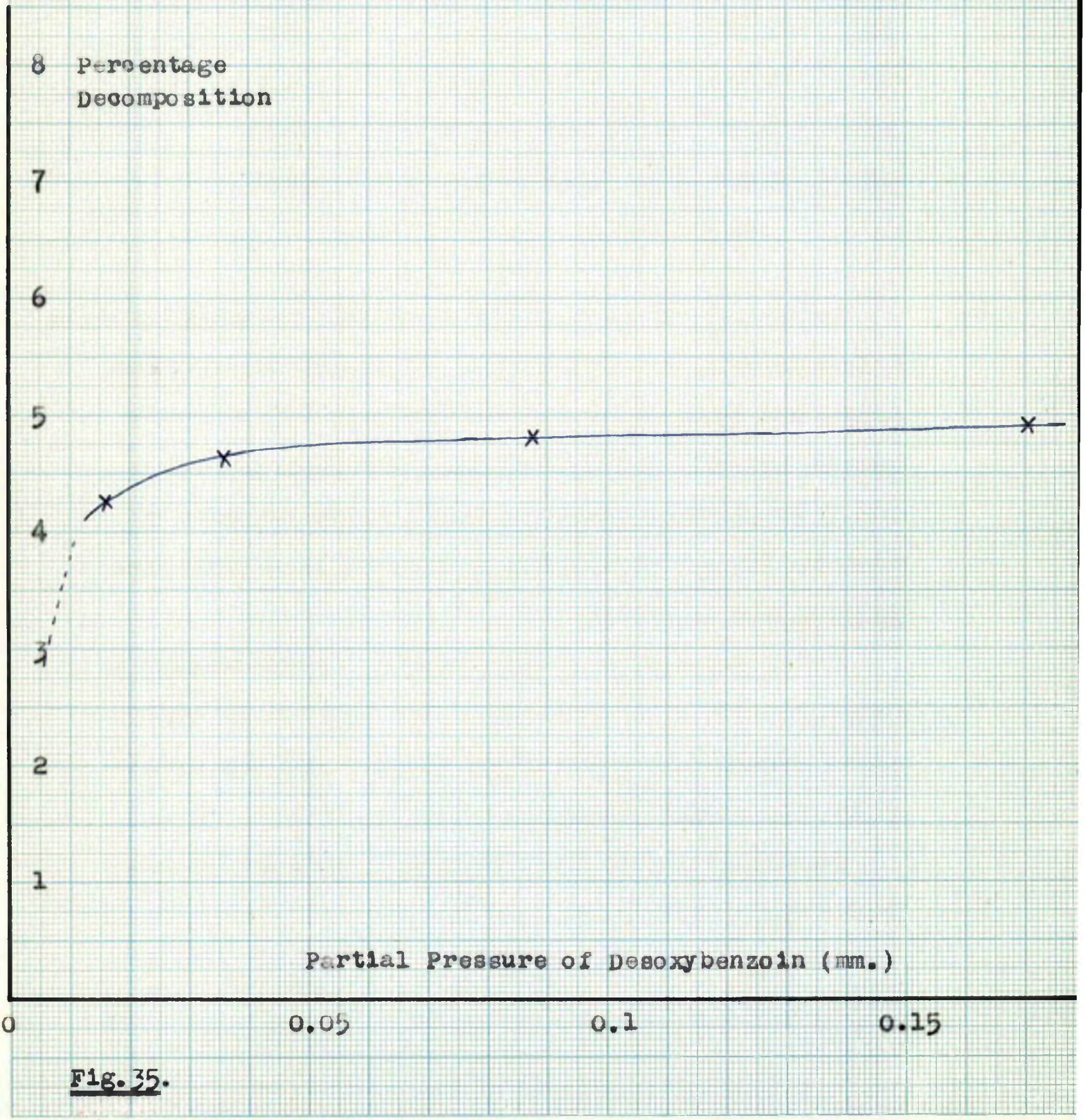


Fig. 35.

TABLE 25

Expt.	Contact time (secs)	P_{des} (mm)	P_{tol} (mm)	% decomposition
132	0.395	0.17	1.14	4.90
135	0.372	0.0375	1.22	4.80
134	0.350	0.056	1.34	4.66
135	0.332	0.016	1.41	4.25
All at 601°C.				

The plot of per cent decomposition against the partial pressure of deoxybenzoin, shown opposite, is a horizontal straight line, showing that the decomposition was first order with respect to deoxybenzoin under these conditions. The slight fall-off in rate at low partial pressure is possibly due to the number of collisions being insufficient to maintain the first order rate.

Variation of contact time.

If the decomposition of deoxybenzoin to carbon monoxide is first order, and if the free radicals are caught by the toluene without complication, a plot of per cent. decomposition against contact time should be linear.

Experiments were performed to verify if this was the case (at 589°C).

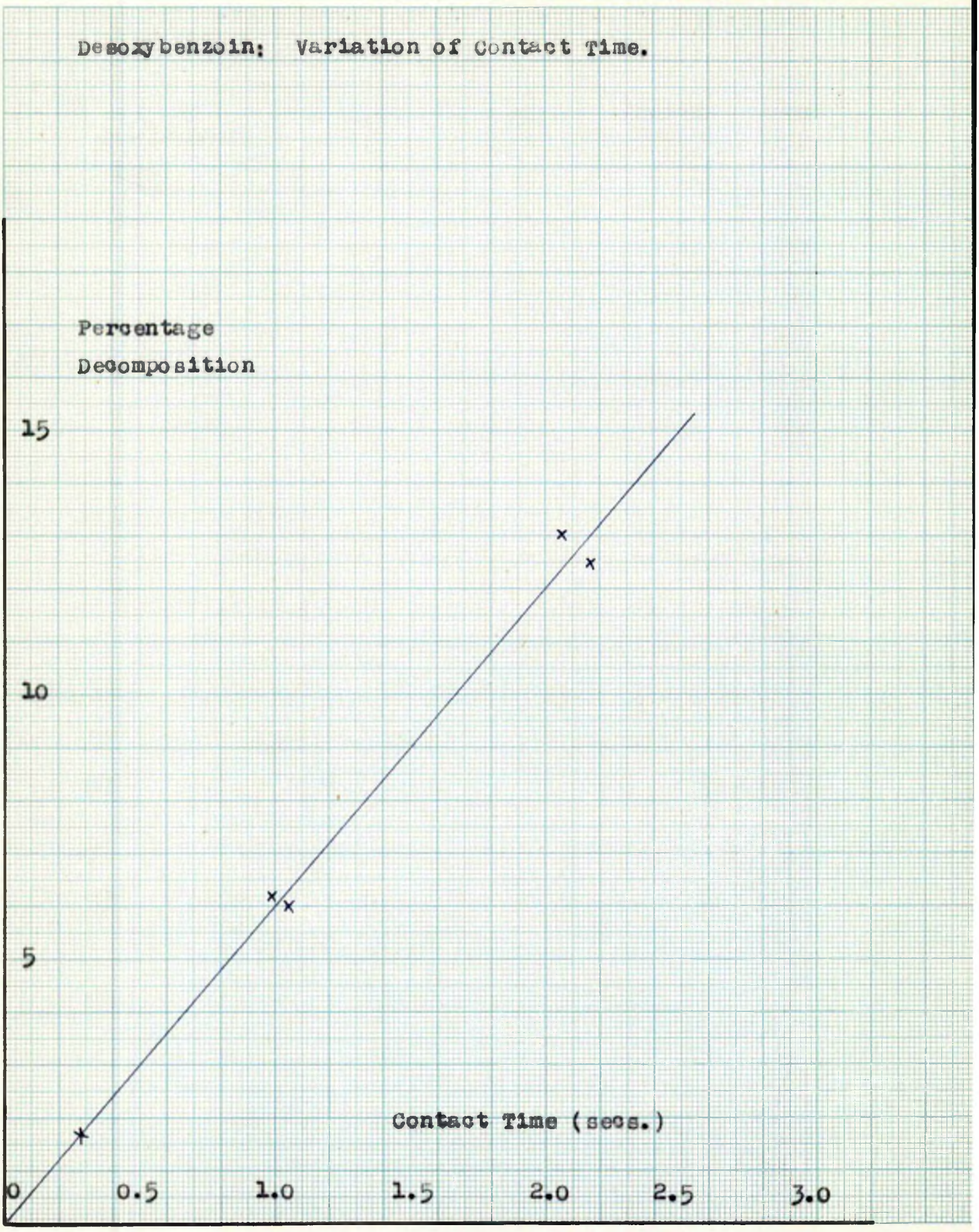

Desoxybenzoin: Variation of Contact Time.
Percentage
Decomposition
15
10
5
Contact Time (secs.)
0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 37.

TABLE 26

Exp't.	Contact time (secs)	P_{des} (mm)	$P_{tol.}$ (mm)	% decomposition
126	0.292	0.127	1.12	1.77
127	1.02	0.077	1.84	6.05
128	1.00	0.51	1.80	6.10
129	2.05	0.105	1.56	15.10
130	2.16	0.307	0.92	12.80

The plot of per cent. decomposition against contact time opposite shows a linear relationship between the two quantities, even for (p toluene / p deoxybenzoin) ratios as low as 1.81, and for per cent. decompositions as high as 15.1.

These results suggest that the mechanism of the decomposition is:

$$PhCOCHCl_2Ph \rightleftharpoons PhCO\cdot + PhCHCl_2\cdot \quad (1)$$

followed by $PhCO\cdot \rightleftharpoons Ph\cdot + CO$ (rapid) (2)

and $Ph\cdot + PhCH_3 \rightleftharpoons PhH + PhCHCl_2\cdot$ (3)

and $\rightleftharpoons PhCHCl_2Ph + H\cdot$ (4)

or $CH_3.C_6H_4.Ph$ etc.

$$2PhCHCl_2\cdot \rightleftharpoons (PhCHCl_2)_2 \quad (5)$$

TABLE 37

Expt.	Temp. (°C)	Contact time (secs)	% decomposition	$\log_{10} k_{uni}$	$10^3/T$ (°K)
124	615	0.355	6.00	$\bar{1}.365$	1.133
125	614	0.402	6.90	$\bar{1}.251$	1.137
126	601	0.396	4.80	$\bar{1}.096$	1.144
130	601	0.395	4.52	$\bar{1}.065$	1.144
131	601	0.396	4.10	$\bar{1}.051$	1.144
132	601	0.395	4.90	$\bar{1}.104$	1.144
135	589	0.392	1.77	$\bar{2}.739$	1.160
127	589	1.02	6.05	$\bar{2}.767$	1.160
128	589	1.00	6.10	$\bar{2}.790$	1.160
133	571	0.365	2.19	$\bar{2}.606$	1.185
134	571	0.377	1.95	$\bar{2}.551$	1.185
136	555	0.597	1.04	$\bar{2}.272$	1.208
138	555	0.576	0.915	$\bar{2}.206$	1.208
137	555	0.590	1.00	$\bar{2}.255$	1.208
139	555	0.575	0.559	$\bar{3}.701$	1.241
139	521	0.72	0.37	$\bar{3}.712$	1.289
140	516	0.396	0.203	$\bar{3}.654$	1.297
141	515	0.605	0.141	$\bar{3}.567$	1.272

Desoxybenzoin: Graph of Log.$k_{uni.}$ vs. $10^3/T$ (K)

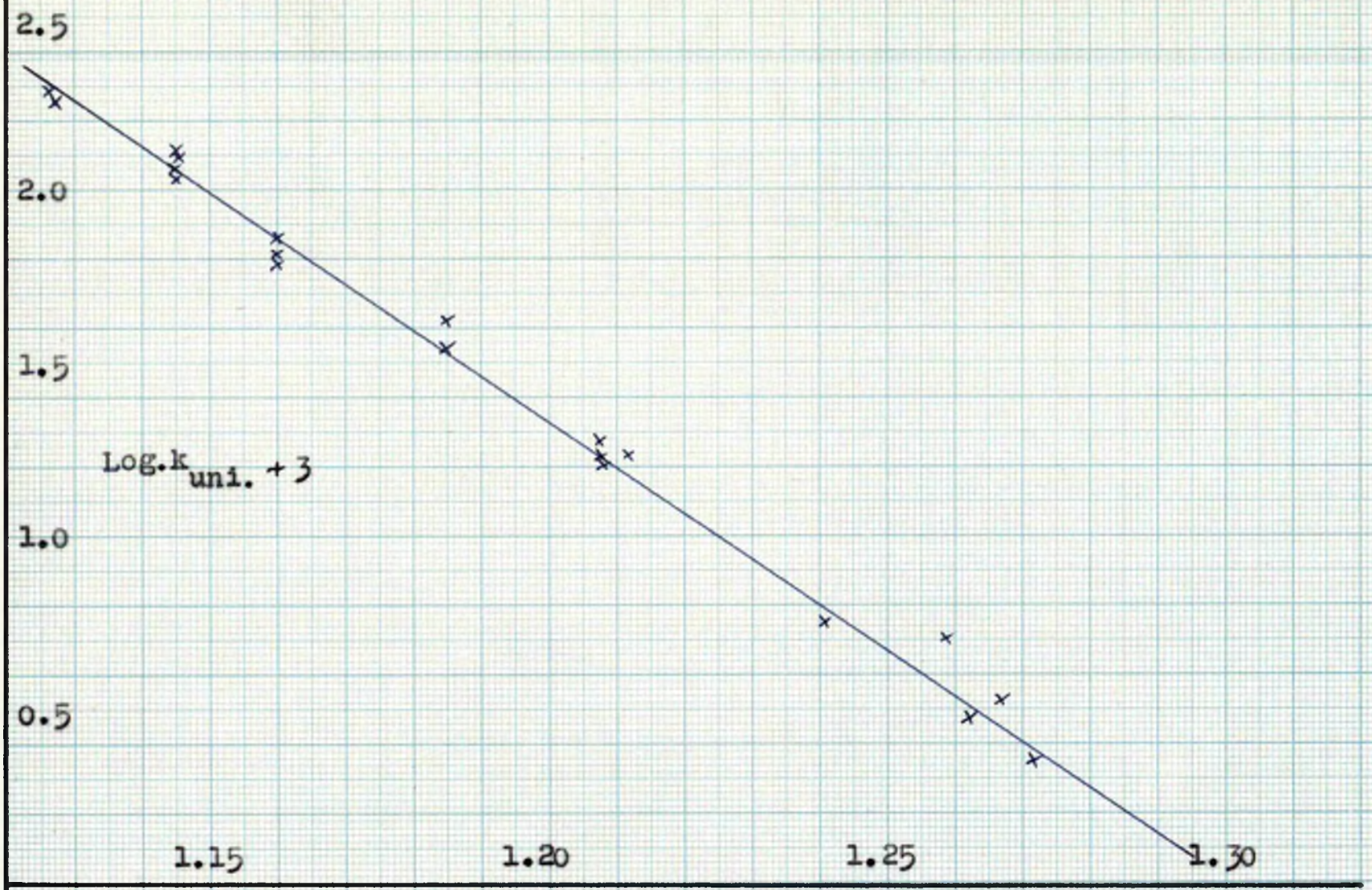


Fig. 38.

Measurement of the amount of carbon monoxide produced by decompositions carried out over a range of temperatures should lead to an experimental activation energy which could be attributed to the bond dissociation energy of the central C-C bond.

Temperature coefficient determination.

Experiments were performed at varying temperatures, and other variables were kept constant as far as possible. To prevent formation of benzophenone and other carbonyl-containing by-products, an excess in partial pressure of toluene over deoxybenzoin of about ten was maintained. The results of these experiments, with earlier relevant data, are tabulated opposite. The plot of $\log_{10}k$ against $10^3/T$ is also shown opposite, and is seen to be a straight line. From the points on this line, using the minimum squares method, we can deduce the activation energy E as 59.8 kcal/mole, and $\log_{10}A$ as 14.10. Before any meaning could be attached to this activation energy, tests were carried out to make sure that the decomposition was not complicated by surface reaction.

Heterogeneity test.

The same pyrex furnace, with removable glass liners and hence variable surface area / volume (S/V) ratio, was used as for the benzil experiments. The results of the experiments are tabulated below:

Desoxybenzoin; Test for Surface Reaction.

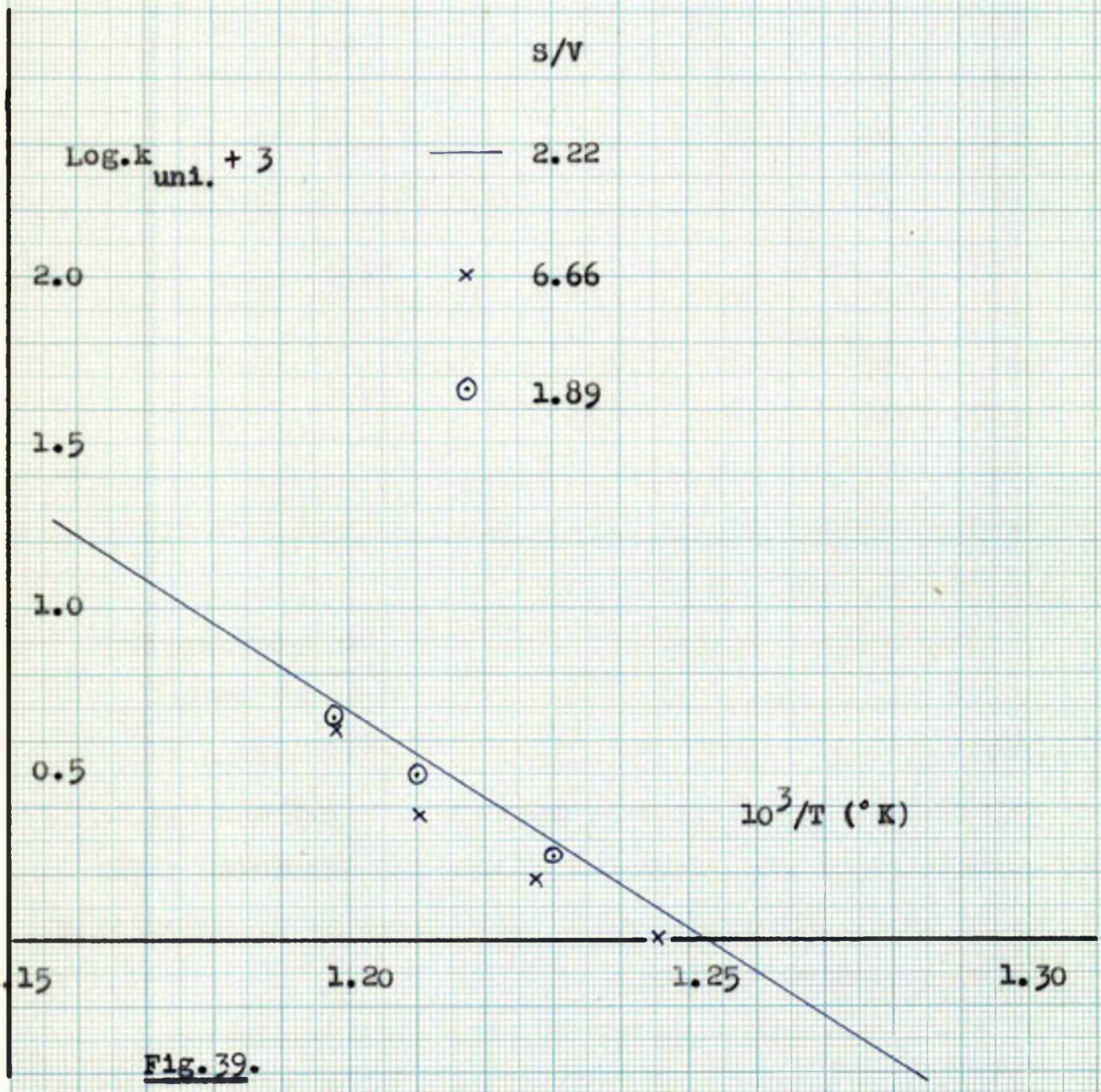


Fig. 39.

TABLE 28

Expt.	Temp. (°C)	Contact time (secs)	S/V	$\log_{10}k_{uni}$	$10^3/T$ (°K)
(a) both linears fitted.					
143	500	0.610	6.66	5.008	1.394
145	511	0.513	6.66	5.130	1.376
144	521	0.503	6.66	5.304	1.359
145	529	0.345	6.66	5.659	1.347
(b) no linears.					
146	509	0.675	1.69	5.249	1.379
147	521	0.655	1.69	5.500	1.359
148	529	0.71	1.60	5.660	1.347

The temperature range could not be extended any higher without softening the pyrex furnace.

When $\log_{10}k_{uni}$ was plotted against $10^3/T$, the points are seen to fall near to the same line, irrespective of the S/V ratio. Since this ratio was varied by a factor of more than three, there must be little surface effect. Again the small difference in position between these points and the data from experiments in the silica furnace (S/V = 3.23) may be due to errors in the estimation of the "hot" length of the furnace.

The decompositions carried out in the silica furnace were homogeneous and the experimental activation energy could be assigned

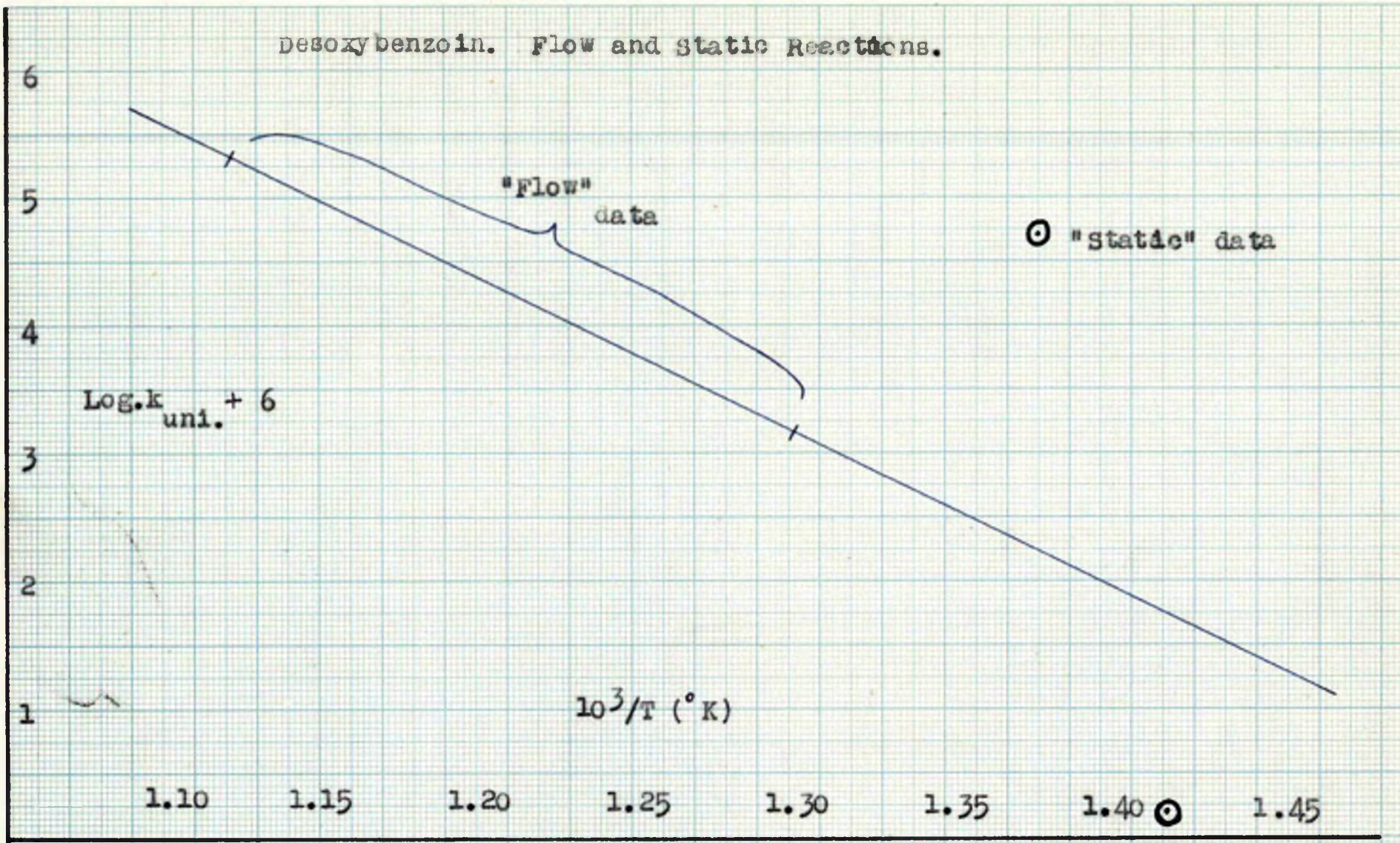

Desoxybenzoin. Flow and Static Reactions.
6
5
4
3
2
1
"Flow" data
"static" data
Log.k uni. + 6
10³/T (°K)
1.10
1.15
1.20
1.25
1.30
1.35
1.40
1.45

Fig.40.

to the bond dissociation energy for the initial split.

$PhCOCH_2Ph$ = $PhCO-$ + $PhCH_2-$

i.e. 69.8 k cal/mole.

Static reactions.

As for benzil, it was thought that static reactions would allow the temperature range to be extended, and an experiment was carried out in a reaction bulb.

Expt.	Temp. (°C)	Contact time (secs)	P_{dbe} (mm)	P_{tol} (mm)	% decomposition	$\log_{10}k_{uni}$	$10^3/T$ (°K)
149	451	260	57.0	532	2.55	6.235	1.420

When this datum is plotted on the same graph as the temperature coefficient data from the flow experiments, the rate of decomposition in the static system is seen to be about fifteen times slower than the flow reaction rate (graph opposite).

Infra-red inspection of the involatile products of the static experiments described, and of several other qualitative experiments carried to different conversion showed a small carbonyl band in the same region as that for benzophenone, and a carbonyl band at about 6.1μ. The compound giving this absorption band was not identified but from the position of the band, the carbonyl group must be in a highly conjugated system. e.g. A condensed ring quinone, like pyrene quinone, has its carbonyl band at 6.10μ.

Under the static conditions, the partial pressure of

desoxybenzoin was about 600 times greater than under the flow conditions, the concentration of radicals would be much higher, and the chance of radical-radical collision correspondingly greater. The benzyl radicals would be expected to be reasonably stable under these conditions, and there might be recombination of benzoyl radicals with these benzyl radicals to give desoxybenzoin again. The presence of benzophenone suggests the reaction of phenyl and benzoyl radicals. Careful inspection both by direct and reference techniques showed that benzil was not present in any of the static reaction residues, which suggests that the benzoyl radicals do not live long enough under these conditions to collide and recombine.

Summary.

Experiments with desoxybenzoin/toluene mixtures in a static system did not provide more data for the temperature coefficient plot because of complicating free radical reactions giving carbonyl-containing products. The absence of benzil in the products shows that at this temperature (431°C) benzoyl radicals are not stable enough to combine.

HYDROGEN IODIDE AS A RADICAL REMOVER.

The thermal decomposition of iodine has been extensively studied. Much of the early work was carried out by Bodenstein who elucidated the mechanism of decomposition as bimolecular and found that the rate constant is given by

$$k = 10^{15.9} \exp(-44000/RT) \text{ mole}^{-1}\text{ c.c. sec}^{-1}$$

Taylor and Crist[68] applied corrections for the hydrogen diffusing through the vessel. Kistiakowsky[69] investigated the thermal decomposition over a wide pressure range by a similar technique to Bodenstein, and the reaction appeared to be homogeneous and bimolecular.

In 1867, Butlerow[70] discovered that alkyl iodides react with hydrogen iodide in a similar way to that of hydrogen iodide itself. Ogg[71] followed the rate of production of iodine by the absorption of light and found that though the overall reaction is second order and represented by

$$RI + HI = RH + I_2 ,$$

decomposition by two mechanisms takes place:

(a)	$RI + HI = RH + I_2$		(1)
(b)	$RI = R + I$		(2)
	$R + HI = RH + I$		(3)
	$R + I_2 = RI + I$		(4)
	$I + I + M = I_2 + M$		(5)

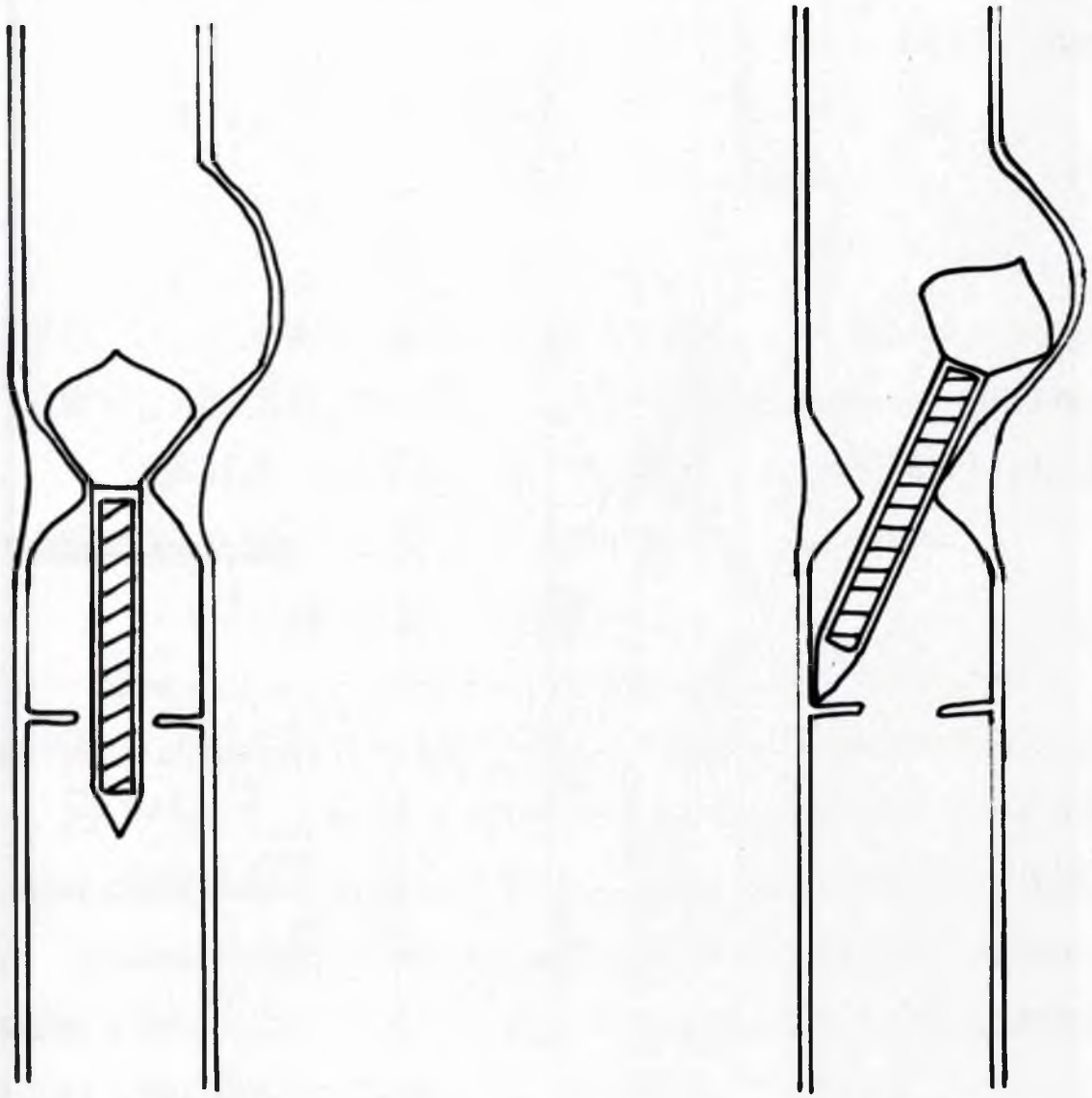
Reaction (8) of the second mechanism illustrates the possible use of hydrogen iodide as an agent for detecting, removing or estimating free radicals.

From the work of Bodenstein we can deduce that at low concentrations, the thermal decomposition of hydrogen iodide alone will be quite slow, since the number of collisions will be small. However, since the H - I bond is so weak, it should readily be broken by reaction with a free radical, if any of these are present. The reaction of a radical with a molecule of hydrogen iodide would yield an atom of iodine and, provided the temperature or hydrogen iodide pressure were not as high as to cause an appreciable background decomposition of hydrogen iodide, measurement of the iodine yield would give an estimate of the number of radicals removed.

Hydrogen iodide was used in the department by Downs[72] and Gow,[25] in the decomposition of iodides, and found to be an extremely effective radical remover.

Inspection of the products of decomposition of benzil and deoxybenzoin in the presence of excess toluene by infra-red spectroscopy showed no evidence for the removal of the benzoyl radical, by a hydrogen extraction reaction with the toluene. It was thought worth while to decompose benzil in excess hydrogen iodide to see if this would give a similar mechanism to that in the presence of toluene or whether the weaker bond attaching the hydrogen atom in hydrogen iodide would allow a hydrogen extraction reaction with the benzoyl radical.

HI CUT-OFF VALVE



CLOSED

OPEN

Fig. 41.

If all the benzoyl radicals decompose, as is believed to be the case for the benzil reaction in excess toluene, the products would be expected to be benzene and carbon monoxide in equimolar amounts, and half as many moles of iodine.

$$Ph\,CO- \;=\; Ph- + CO$$

$$Ph- + HI \;=\; PhH + I$$

$$I + I + M \;=\; I_2 + M$$

If some or all of the benzoyl radicals react with hydrogen iodide, benzaldehyde might be expected as a product, and more gm-atoms of iodine than moles of carbon monoxide would be expected.

Apparatus and Experimental Technique for Experiments with Hydrogen Iodide.

Hydrogen Iodide has been shown to decompose much more readily on the surfaces of gold[73] and platinum[74] than in the homogeneous phase, and tests with stainless steel balls as used in the cut-offs for benzil decompositions in excess toluene showed that these were attacked by hydrogen iodide, with the production of iodine. The high temperature of the heated lines (120°C) made the use of a solenoid type valve difficult, so steel valves enclosed with glass envelopes were made, to be operated by an external magnet. A diagram of one of these valves is shown opposite. An additional modification to the original flow apparatus was required to prevent the hydrogen iodide passing through the hot benzil valve (as the toluene had done) and attacking it. The apparatus was adapted for split flow, as is

BY-PASS SYSTEM FOR HI INJECTION

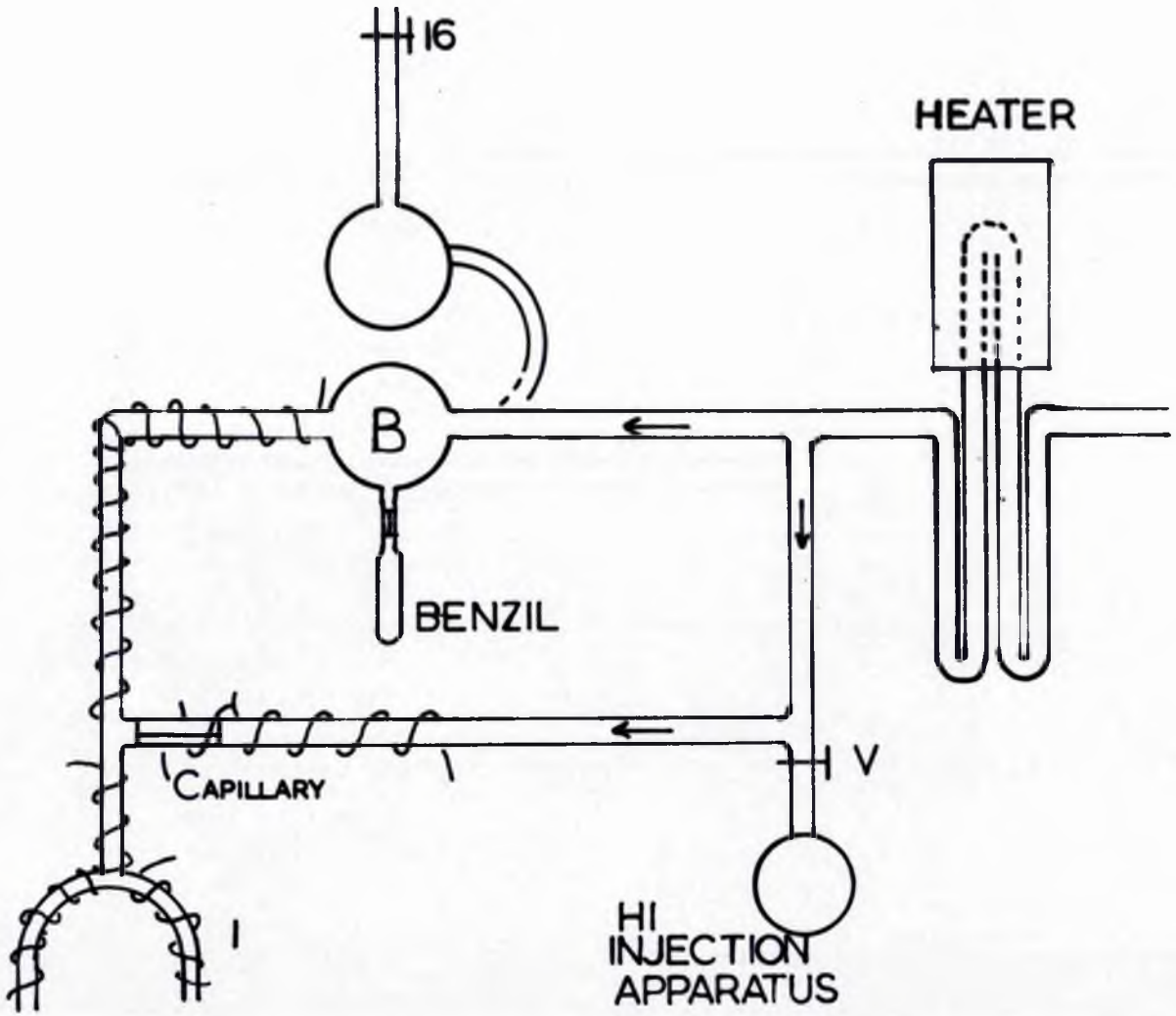


Fig.42.

HI INJECTION APPARATUS

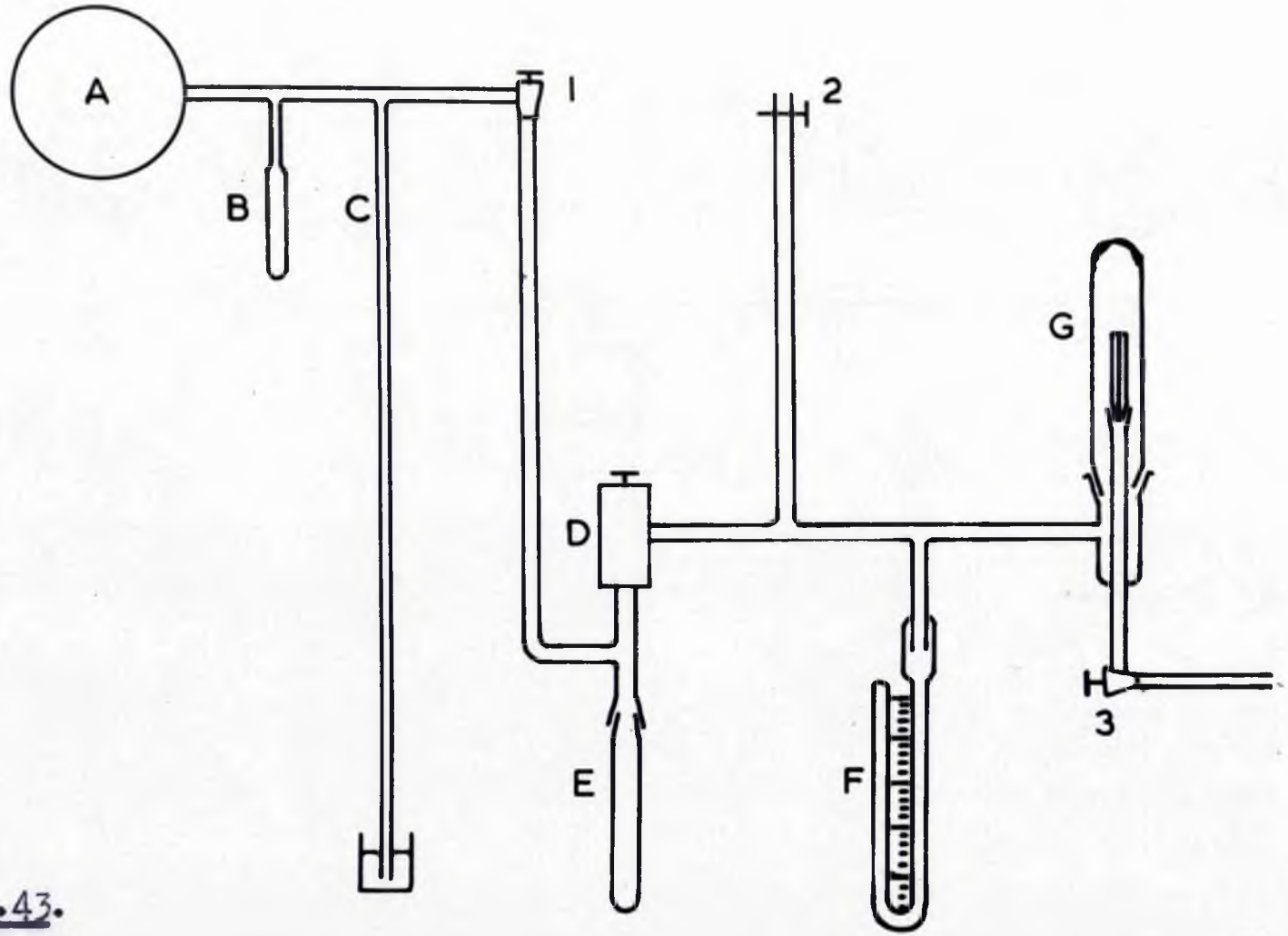


Fig.43.

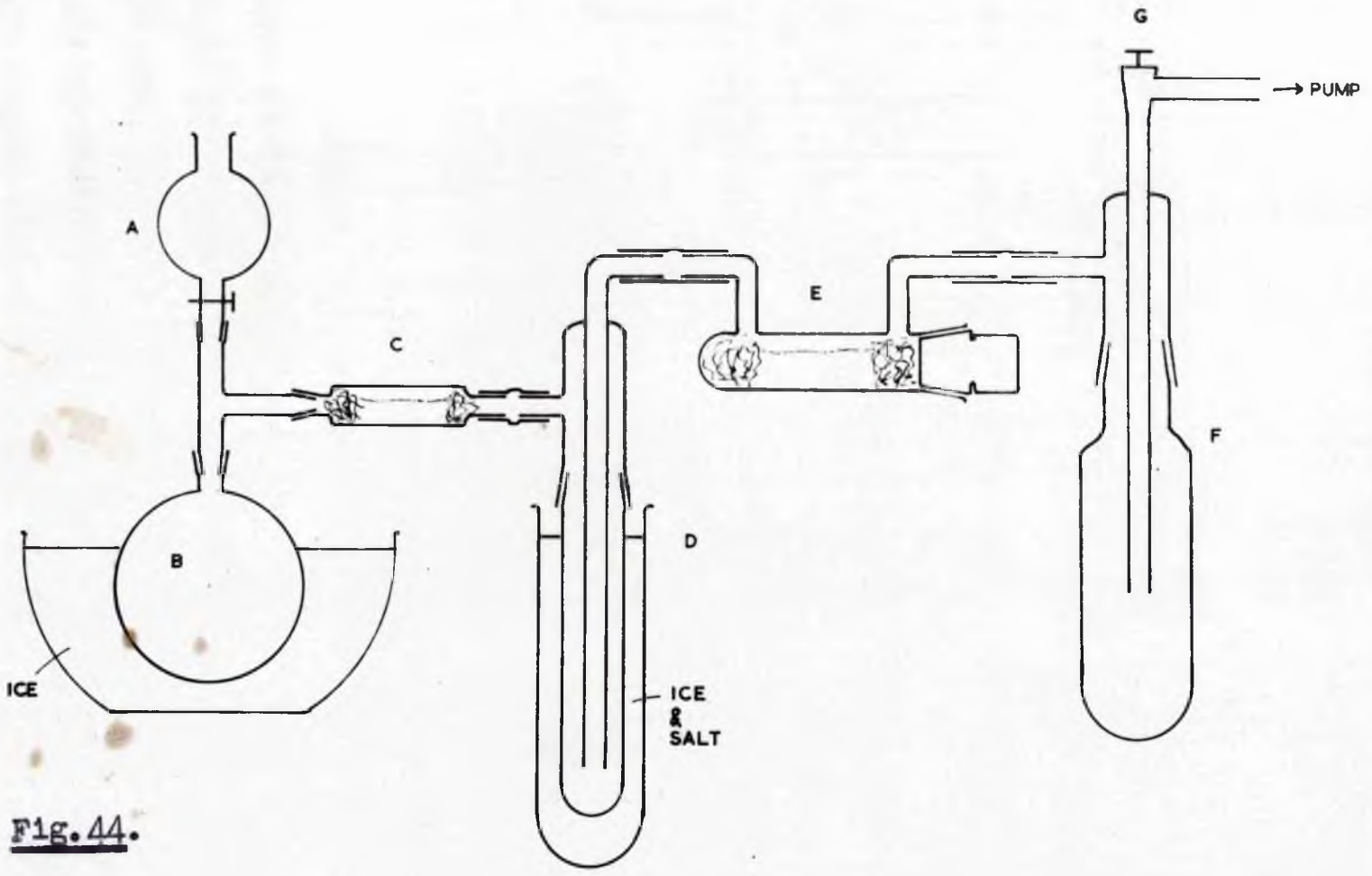


Fig. 44.

[Fig. 42]

shown in the diagram opposite so that hydrogen iodide did not come into contact with the hot benzil valve.

Injection of the reactants.

Benzil.

This was injected in the same way as for the decompositions in the presence of excess toluene.

Hydrogen iodide.

A diagram of the apparatus for the storage and injection of hydrogen iodide is shown opposite. [Fig. 43] The gas was normally stored in the vessel A and for an experiment, some was distilled down into the liquid-oxygen-cooled container E. Tap 1 was then closed, and the apparatus was pumped out through tap 2. A solid carbon dioxide-acetone bath was then placed round the container E and the fore-pressure of hydrogen iodide read on the manometer F and adjusted with the needle valve D. When the fore-pressure was steady and correct, hydrogen iodide was injected into the flow-stream through the interchangeable capillary C by opening tap 3.

The preparation and purification of hydrogen iodide.

[Fig. 44]

A diagram of the apparatus for the preparation is shown opposite. The 700 ml flask B was half-filled with phosphorus pentoxide, and suction from a water pump and intermediate liquid-oxygen-cooled water trap, was applied at G. A liquid oxygen bath was placed round the trap F, and 55% hydrogen iodide solution was dripped slowly into flask B. Hydrogen iodide gas was evolved and was drawn through the

apparatus by the applied suction. The ice and salt-cooled bath D removed iodine from the gas stream. The hydrogen iodide gas was dried by phosphorus pentoxide at C and E, and froze to the solid in the trap F.

The hydrogen iodide was subsequently freed from traces of iodine, water and other less volatile impurities by repeated distillation from a trap at -30°C to one at -180°C. Since the decomposition of hydrogen iodide is catalysed by light, it was stored, as the gas, in opaque flasks.

Experimental procedure.

Since hydrogen iodide itself decomposes slightly to iodine at the temperatures used, for each complete experiment a blank run with hydrogen iodide alone was first carried out.

Collection of the products.

(a) Hydrogen iodide blank.

The collection trap F was cooled in liquid oxygen and glass wool inside the trap increased the thermal contact and mixing and hence the freezing efficiency.

(b) Benzil decomposition.

For the experiment the appropriate products trap F was cooled in a solid carbon dioxide-acetone bath to collect the iodine and benzil, and the hydrogen iodide passed by, to be collected later by the liquid oxygen-cooled trap J.

Separation and analysis of the products.

(1) Hydrogen iodide from the blank experiments was distilled into previously out-gassed methanol in the subsidiary trap G over liquid oxygen, from the main products trap F over a -80°C bath. The iodine remaining in the trap F was then titrated.

(2) The gaseous products were analysed as for the products of the experiments with benzil in excess toluene.

(3) Any products more volatile than iodine were distilled from a -40°C bath round the products trap F into the trap G over liquid oxygen. The contents of trap G were then dissolved in carbon tetrachloride, shaken with aqueous thiosulphate to remove iodine, and submitted to ultra-violet spectroscopic analysis.

(4) Ultra-violet spectroscopic analysis of the involatile products was very difficult because of the large amounts of iodine interfering.

Calculation of the amount of iodine from a hydrogen iodide blank experiment.

For the decompositions of benzil, in excess toluene, to determine the temperature coefficient, the partial pressure of benzil used was about 0.1 mm. mercury, and since hydrogen iodide has been shown to be a much more efficient radical catcher than toluene, a ten times excess in partial pressure of hydrogen iodide over benzil should be quite sufficient to trap all the radicals formed, for conversion less than 10 per cent.

From the experiments with benzil, and deoxybenzoin in toluene, the highest temperature required would be 615°C., which gave 6.5

per cent. conversion for deoxybenzoin.

For 1 mm. pressure of hydrogen iodide at 615°C (888°K) the concentration of hydrogen iodide

$$[HI] = 1 \times \frac{1}{760} \times \frac{273}{888} \times \frac{1}{22.4} = \underline{1.31 \times 10^{-6} \text{ moles/litre}}$$

The rate of decomposition of hydrogen iodide = $k [HI]^2$

where $k = 10^{10.9} \cdot e^{-44000/RT}$ moles. l. sec^{-1}

$$\log_{10} k = 10.9 - \frac{44000}{4.57 \times 888} = 10.90 - 10.80$$

$$= 0.10$$

Rate of decomposition $= k [HI]^2$

$$= 10^{0.1} \cdot (1.31 \times 10^{-6})^2$$

$$= 3.25 \times 10^{-9.9}$$

$$= \underline{4.09 \times 10^{-10} \text{ moles. l. sec}^{-1}}$$

The hot furnace volume is 250 ml, contact time say 0.5 sec., and duration of an experiment say, 10 minutes.

Rate of flow of reactant = 0.500 litre/sec.

moles of iodine formed in an experiment

$$= 4.09 \times 10^{-10} \times 10 \times 60 \times 0.500$$

$$= \underline{1.37 \times 10^{-7}}$$

If the mechanism for the deoxybenzoin decomposition were

$$PhCOCH_2Ph = PhCO\cdot + PhCH_2\cdot$$

and if all the benzoyl radicals decomposed,

$$PhCO\cdot = Ph\cdot + CO$$

and all the phenyl radicals were caught

$$Ph\cdot + HI = PhH + I$$

one mole of iodine would be expected for each two moles of carbon monoxide.

At 0.1 mm. partial pressure, the concentration of deoxybenzoin

$$[\text{deoxybenzoin}] = 0.10 \times \frac{1}{760} \times \frac{273}{303} \times \frac{1}{22.4}$$

$$= \underline{1.61 \times 10^{-6} \text{ moles/litre.}}$$

The total rate of gas flow = 0.500 litres/sec.

Therefore, in a 10 minute experiment, the moles of deoxybenzoin used = $1.61 \times 10^{-6} \times 0.50 \times 10 \times 60 = 6.05 \times 10^{-4}$.

As stated, when decomposed under the conditions outlined in excess toluene, the deoxybenzoin went to 6.5 per cent. conversion; so the moles of carbon monoxide expected under these conditions would be

$$= \frac{6.5 \times 6.05 \times 10^{-4}}{100} = \underline{3.93 \times 10^{-5}}$$

Therefore, in catching the radicals from the decomposition of deoxybenzoin at 615°C, under the conditions described and in the presence of excess hydrogen iodide, the amount of iodine formed would be at least $= \frac{1}{2} \times 3.93 \times 10^{-5}$

$$= \underline{1.97 \times 10^{-5} \text{ moles iodine}}$$

The decomposition of hydrogen iodide alone could produce only 1.37×10^{-7} moles iodine which is too small to prevent measurement of the iodine in the actual experiment giving an accurate indication of the number of radicals which reacted with the hydrogen iodide.

Ultra-Violet absorption curve for Volatile Products of the decomposition of Benzil in excess Hydrogen Iodide.

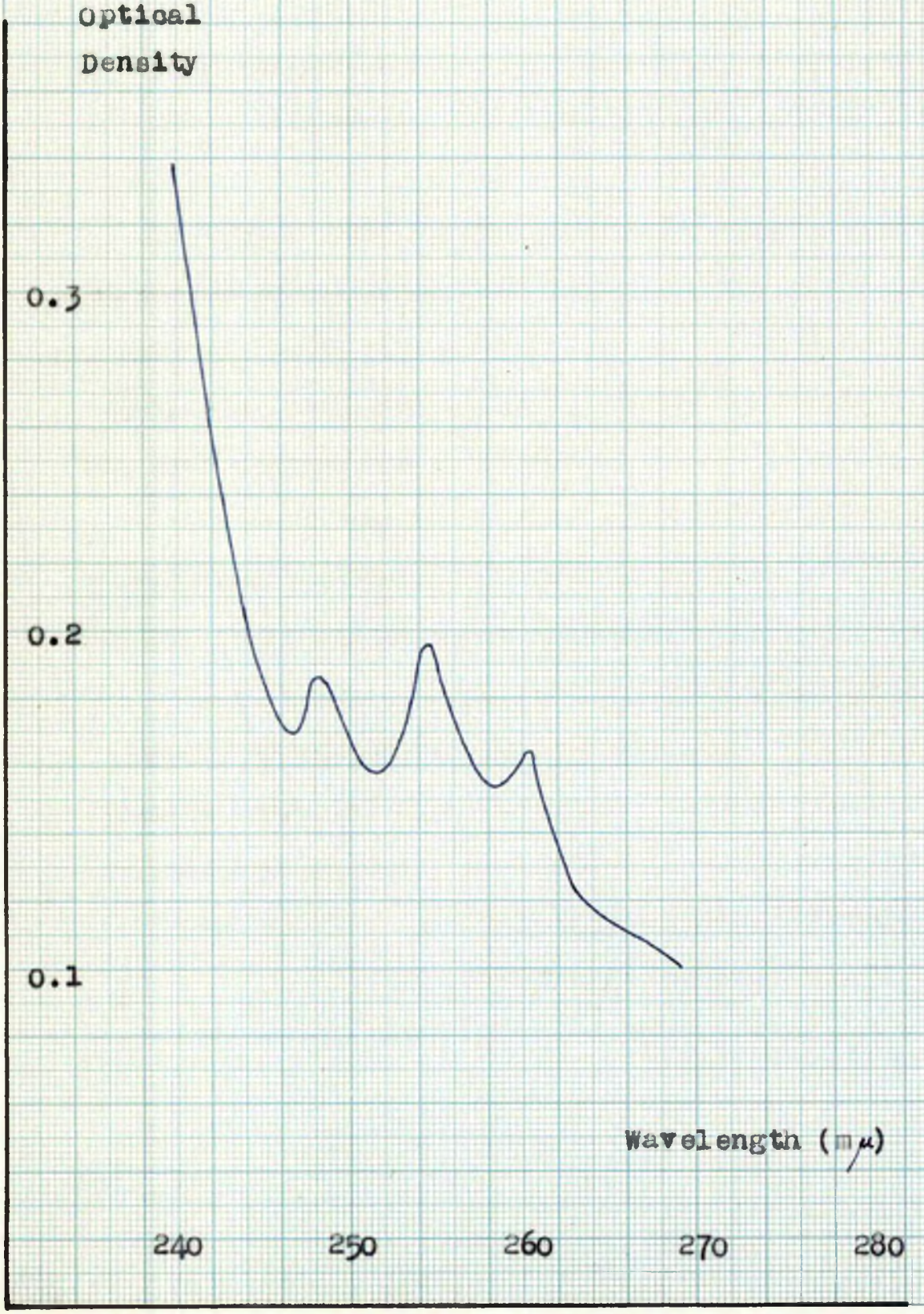


Fig.45.

A blank experiment with III alone was however, performed before each run, and correction made for the iodine formed.

Experimental Results.

(a) With benzil.

Several rough experiments at high decomposition were first performed to develop methods of separation and analysis of the products.

When the volatile products were distilled into a trap over liquid oxygen from a trap at $-40^{\circ}C$, dissolved in carbon tetrachloride and, after removal of iodine, subjected to ultra violet spectroscopy, absorption bands characteristic of benzene were found, as is shown on the graph opposite. The presence of benzene suggests that some at least of the benzoyl radicals decompose to phenyl radicals.

Absorption of the solvent prevented a search for benzaldehyde absorption bands in the ultra-violet region for the solution of the volatile distillate in carbon tetrachloride.

Because of interference by the iodine absorption in the ultra violet it was not possible to measure directly the amount of benzil left after an experiment. The benzil valve was calibrated before each experiment with the furnace by pass trap. Two experiments at widely varying temperatures were performed:

Benzil: Decomposition in excess Toluene and in excess Hydrogen Iodide.

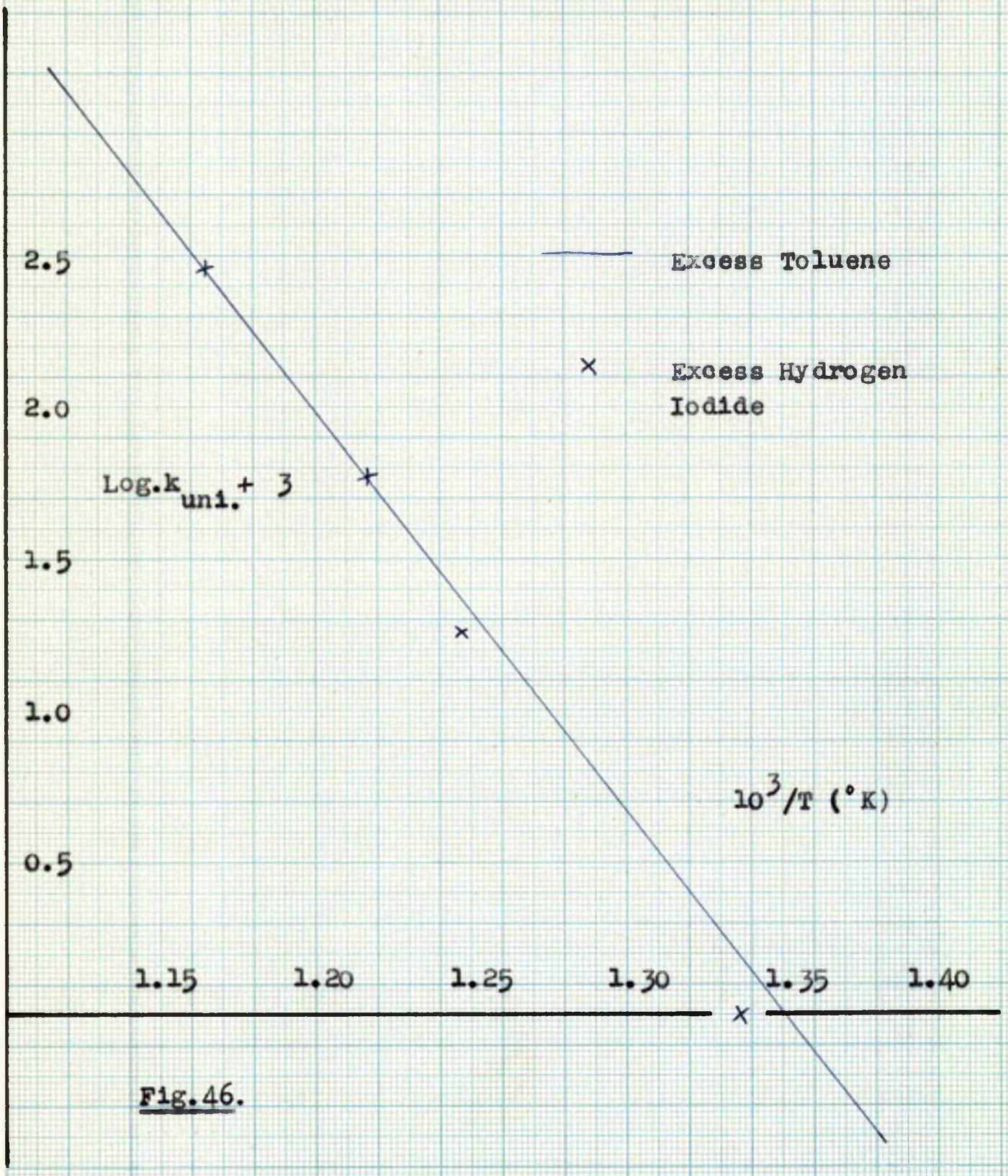


Fig.46.

TABLE 29

Expt.	Temp. (°C)	Contact time (secs)	gm.atoms iodine	moles carbon monoxide	$\log_{10}k_{uni.}$	$10^5/T$ (°K)
150	326	0.54	2.36×10^{-4}	5.27×10^{-5}	$\bar{1}.440$	1.184
151	329	0.64	1.65×10^{-4}	4.54×10^{-5}	$\bar{1}.241$	1.297

The unimolecular rate constant was calculated as for the experiments for benzil decomposition in excess toluene on the basis of two molecules of carbon monoxide per unimolecular split, and when these points are plotted on the same graph, shown opposite, they lie close to the line for the experiments with toluene, though slightly below it.

If the hydrogen iodide were reacting only with phenyl radicals, as toluene appeared to, for each mole of carbon monoxide would be expected one gm.-atom of iodine, but these experiments produced a large excess of iodine over carbon monoxide.

(a) The apparatus was tested exhaustively for leaks in case the hydrogen iodide was being oxidised, but none was found.

(b) Considering the small extent of the bimolecular decomposition of the hydrogen iodide itself at 0.7 mm. pressure, it seemed unlikely that the iodine was the product of a bimolecular reaction between hydrogen iodide and benzil, when the partial pressure of the latter was only about 0.06 mm.

(c) For the above two experiments, it was noted that the (gm.-atom iodine / moles carbon monoxide) ratio was higher at the lower temperature. Further experiments confirmed this variation:

TABLE 50

Expt.	Temp. (°C)	Contact time (secs)	gm.atoms iodine	moles carbon monoxide	$\log_{10}K_{mol}$	$10^3/T$ (°K)
152	547	0.77	4.23×10^{-4}	9.75×10^{-6}	2.735	1.217
153	475	0.81	1.81×10^{-4}	2.16×10^{-6}	4.903	1.387
154	406	0.91	-	-		
			not measurable			

and an alternative tabulation shows it clearly:

TABLE 51

Expt.	Temperature (°C)	(gm.atoms iodine / moles carbon monoxide)
150	536	7.25
152	549	14.4
151	529	56.3
153	475	89.3
154	406	Both iodine and carbon monoxide too little to be measurable.

To find if the iodine produced was proportional to the partial pressure of either benzil, or hydrogen iodide, two further experiments were performed.

TABLE 32

Expt.	Temp. (°C)	moles carbon monoxide	gm.atoms iodine	gm.atoms iodine/ moles carbon monoxide	P_{bz} (mm)	P_{HI} (mm)	% conversion (to carbon monoxide)
155	386	7.10×10^{-5}	4.26×10^{-4}	6.0	0.10	0.70	10.9
156	386	8.40×10^{-5}	2.64×10^{-4}	3.15	0.14	0.26	12.8
150	386	5.27×10^{-5}	2.36×10^{-4}	7.20	0.04	0.70	15.8

Comparison of the results of experiments 155 and 150 suggests that the iodine yield is not directly proportional to the partial pressure of benzil. Comparison of experiments 155 and 156, suggests that the amount of iodine is roughly proportional to the partial pressure of hydrogen iodide used.

If the excess iodine were the product of some kind of chain in the hydrogen iodide (which seemed unlikely), an equimolar amount of hydrogen with the iodine might be expected. For experiment 155 the amount of hydrogen produced was measured by mass spectrometric observation of the carrier gas and 2.6×10^{-6} moles hydrogen were obtained. A repeat experiment produced 4.20×10^{-6} moles of hydrogen and of this, 2.90×10^{-6} moles were observed to come from the decomposition of the first burst at higher pressure as the

hydrogen iodide injection was started. Evidently, the "excess" iodine was not the product of some chain reaction in the hydrogen iodide.

A mechanism was suggested to explain the previous data. It was suggested that an equilibrium is set up between benzil and benzoyl radicals, and that some of the benzoyl radicals are removed by hydrogen iodide, and some decompose to phenyl radicals and carbon monoxide. The full scheme can be written out as follows:

$$PhCOCOPh \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2PhCO\cdot \xrightarrow{k_3} 2Ph\cdot + 2CO$$

$$\downarrow + 2HI \qquad \downarrow + 2HI$$

$$2PhCHO + 2I \qquad 2PhI + 2I$$

The activation energy for benzoyl-recombination would be expected to be small and that for benzoyl attack on hydrogen iodide quite small. The reaction of benzoyl radicals with hydrogen iodide would be facilitated by the relatively high partial pressure of hydrogen iodide. In connection with this mechanism it is worth noting that:

(a) the activation energy for initial split would probably be smaller than that previously deduced from the carbon monoxide production.

(b) if most of the benzoyl radicals reacted with hydrogen iodide, the amount of iodine formed would be expected to be proportional to the square root of the benzil concentration.

(a) the higher ratios for (ga-atoms iodine/ moles carbon monoxide) at lower temperatures could be due to the greater stability of the benzoyl radical under these conditions.

(d) for the experiments for benzil decomposition in excess toluene, the fall-off in the rate of decomposition at high conversion may have been due, in part, to benzoyl recombination.

If the mechanism suggested is the true one, the products of the reaction of benzoyl radicals with hydrogen iodide should be detectable. The obvious product would appear to be benzaldehyde, if this were stable under the reaction conditions. Hinshelwood et alia[76] pyrolysed benzaldehyde in a static system, and showed the overall reaction to be

$$PhCHO \rightarrow PhH + CO$$

However, no quantitative data were recorded.

Two experiments were carried out to find if benzaldehyde was stable under the reaction conditions.

TABLE 35

Expt.	Temp. (°C)	Contact time (secs)	$P_{benzaldehyde}$ (mm)	P_{HI} (mm)	ga.atoms iodine	decomposition (to carbon monoxide)
157	549	0.60	0.23	0.66	5.2×10^{-5}	0.19
158	547	0.59	0.24	0.66	7.8×10^{-5}	0.20

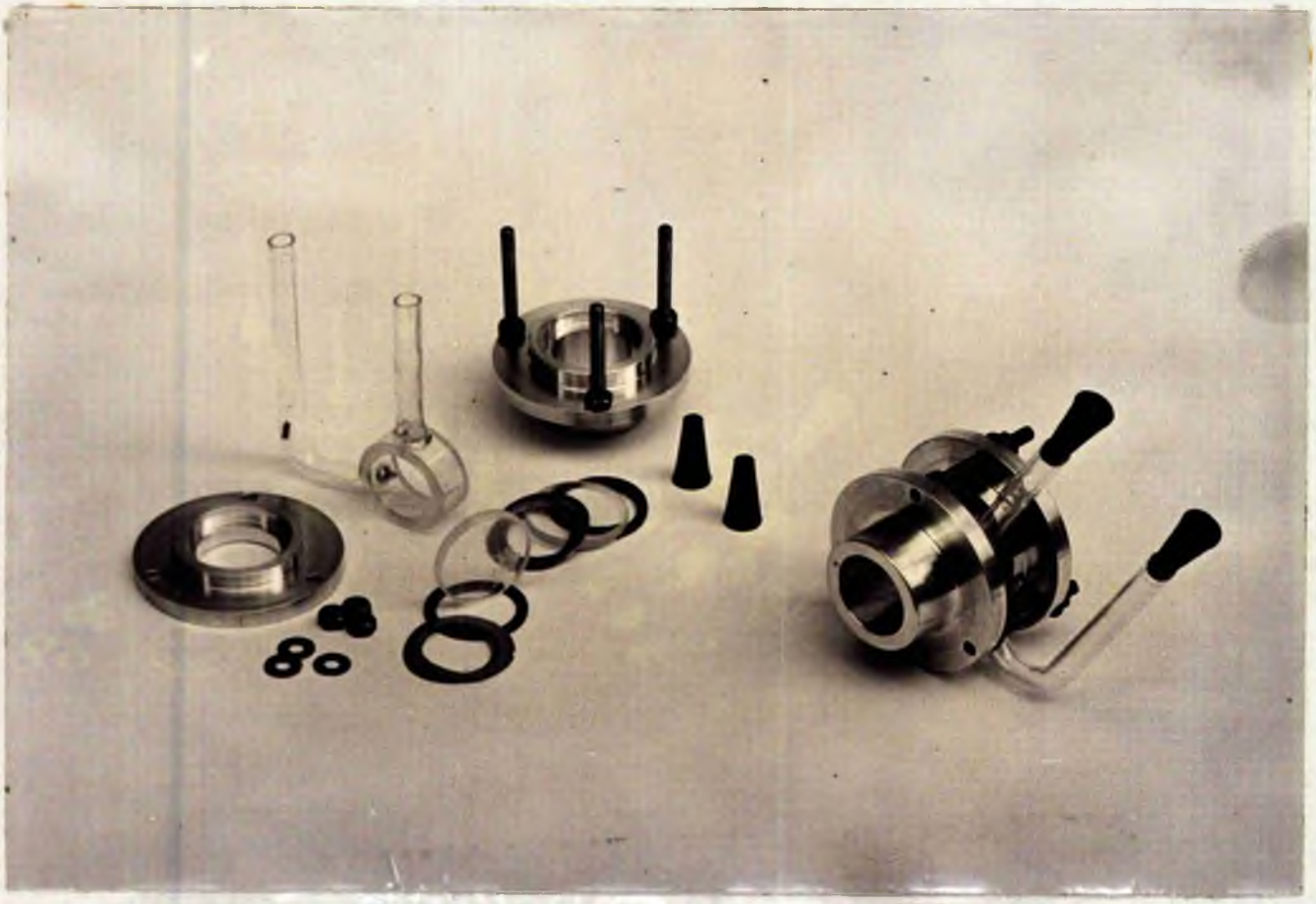


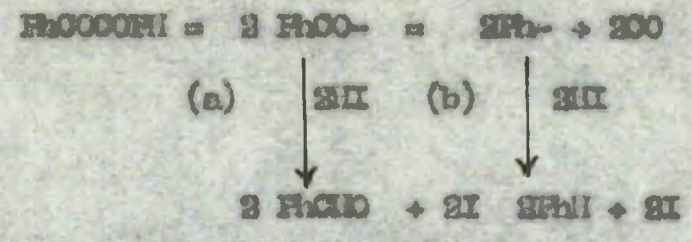
Fig.47.

The low yield of carbon monoxide confirmed the slight decomposition of benzaldehyde under these conditions. The relatively low yield of iodine, though more benzaldehyde was used here than could have been formed in the decompositions of benzil in excess hydrogen iodide, suggests that reaction of benzaldehyde with hydrogen iodide could not explain the large yields of iodine obtained. Since benzaldehyde is stable under these experimental conditions it seems likely that if benzoyl radicals are caught in large amount by hydrogen iodide in the decomposition of benzil in excess hydrogen iodide, benzaldehyde should be found as a product.

Infra-red spectroscopic analysis.

To facilitate handling of the solution of the products, a 1 cm. cell was constructed, as illustrated opposite. The cell had sodium chloride windows, and had a capacity of about 4 ml. Using this cell it was quite easy to resolve the two carbonyl bands for a 10 per cent. mixture (by gram weight) of benzaldehyde in benzil and the strengths of the absorption bands were measured for a calibration.

Inspection of the involatile products of experiment 150 showed that the molar percentage ratio of benzaldehyde to benzil in the products was considerably less than 30. The per cent. conversion of benzil to carbon monoxide for this experiment was 15.8 The proposed mechanism for the production of iodine was:



Since the ratio (gm.atoms iodine/moles carbon monoxide) for the experiment was 7.25, the extent of dissociation of the initial step must be at least 50 per cent., if the excess iodine came from stage (a) of the above mechanism.

Suppose 1 mole of benzil were present at the start. Decomposition to 15.8 per cent. conversion would give 0.276 moles carbon monoxide, and the amount of iodine formed would be 7.25 x 0.276 = 1.26 gm.atoms. 0.276 gm. atoms of this iodine would be produced from stage (b), so (1.26 - 0.276) = 1.00 gm. atoms must be produced by stage (a). This would involve 0.50 moles benzil decomposing to benzoyl radicals which should give 1.0 moles benzaldehyde by stage (a).

In the products then, would be expected 1 mole benzaldehyde and 1.0-(0.5 + 0.158) = 0.362 moles benzil.

Infra-red spectroscopic inspection of the involatile products of experiment 156 showed that, as for experiment 150, there was a much less than 20 per cent. molar ratio of benzaldehyde to benzil.

The products of experiment 155 showed hardly a trace of benzaldehyde, and in the absence of this product in the required amount, the proposed mechanism was discarded.

The presence of some benzaldehyde however, suggests that a small

proportion of the benzoyl radicals do react with the hydrogen iodide.

Though the possibility at first had seemed unlikely, it was decided to test for second order reaction between benzil and hydrogen iodide. The furnace temperature was lowered to a value where decomposition to carbon monoxide was slight, and the partial pressure of hydrogen iodide was varied over a series of experiments.

The shape of the plot of moles iodide produced against the partial pressure of hydrogen iodide should give some indication of the mechanism. If the hydrogen iodide is serving only to react with radicals, the plot should level off at high partial pressures of hydrogen iodide. A second order reaction would be indicated by a linear plot.

The experiments were performed at 500°C at a contact time of about 0.85 secs.

TABLE 34

Expt.	P_{bz} (mm)	P_{HI} (mm)	moles iodine
159	0.059	0.17	2.80×10^{-6}
160	0.04	0.27	1.75×10^{-5}
161	0.035	0.46	3.50×10^{-5}
162	0.03	0.79	4.47×10^{-5}
163	0.042	0.76	1.78×10^{-4}

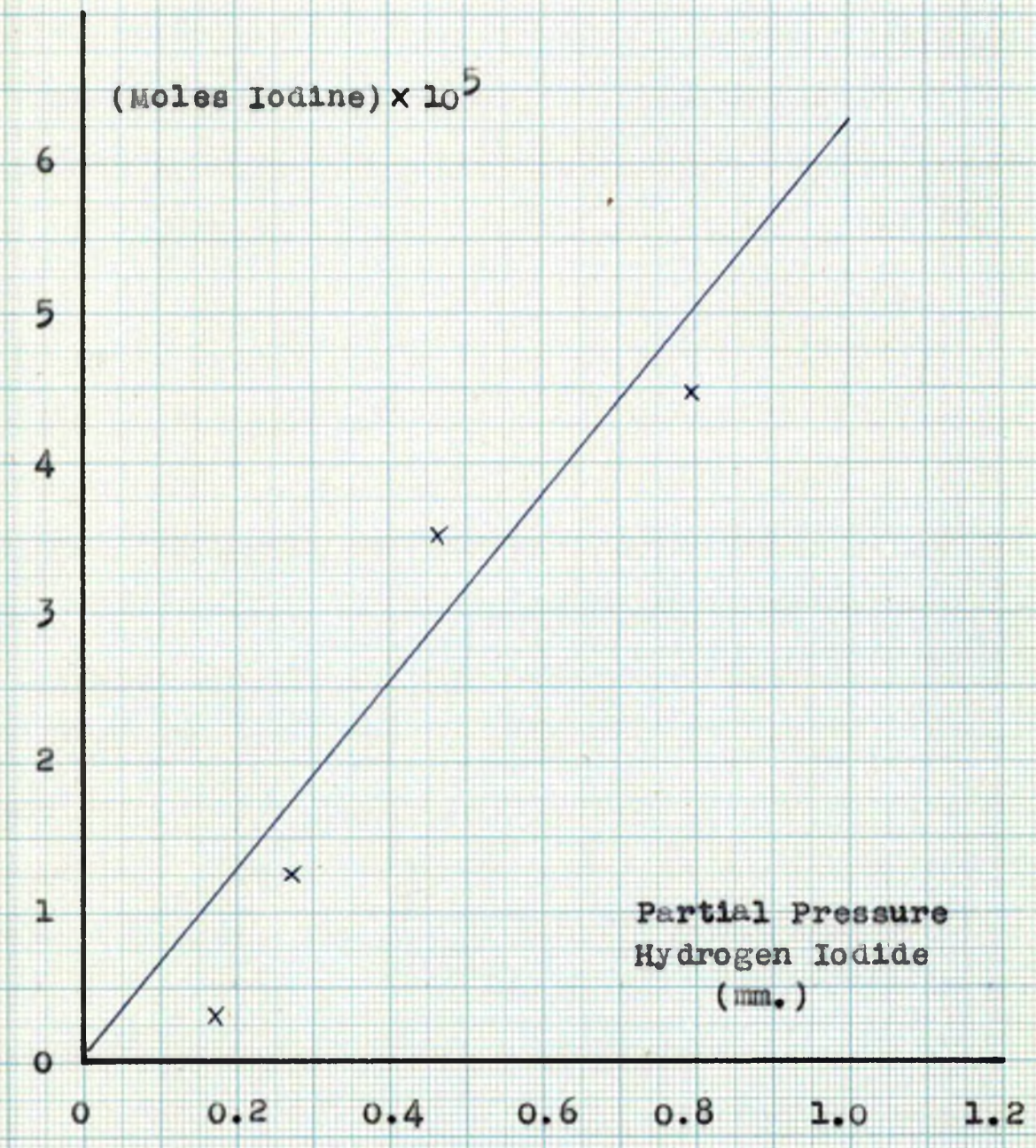

(Moles Iodine) x 10^5
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1.0
1.2
Partial Pressure
Hydrogen Iodide
(mm.)

Fig. 48.

The plot of moles iodine produced against partial pressure of hydrogen iodide approximates to a straight line through the origin, as is shown opposite. This supports the suggestion that the hydrogen iodide reacts with the benzil.

Further Infra-red spectroscopic investigation of the involatile products.

It was noticed that some of the benzil absorption bands disappeared when the carbon tetrachloride solution was diluted. The 1 cm. cell was, therefore, replaced by a 0.8 mm. cell

(a) Range 2.6-3.7μ.

The involatile products of experiments 162 and 165 showed absorption bands at about 3.2 - 3.3μ due to aromatic C-H vibrations, and in addition, two bands at 3.41 and 3.50μ. These latter bands are due to the C-H stretching of methylene groups, which suggests reduction of the benzil.

Comparison of these spectra with those for desoxybenzoin, benzoin, toluene, dibenzyl, stilbene, showed that the spectra of the products had a far greater non-aromatic C-H absorption relative to the aromatic C-H absorption, than even dibenzyl. This suggests that some reduction of the rings to e.g. cyclohexanes was taking place.

A small, broad band at 2.87μ was in the same position as the OH absorption band for benzoin.

Absence of any marked bands at 3.55μ , 3.67μ confirmed the

absence of any appreciable amount of benzaldehyde.

(b) Range 5.0 - 11.0μ.

The application of the reference technique by using benzil as the reference compound showed a broad products absorption band at 5.9 - 6.0μ. This may be due to the carbonyl absorption of several reduced benzils. Bands at 7.6, 7.87, 9.25, 9.36, 9.72, 10.0 and 10.23μ were found, which are characteristic of benzoin.

Analysis of the involatile products of experiments 161 and 162 at the strong absorption band at 10.23μ, showed that they contained about 20 per cent. as much benzoin as benzil.

Summary.

The decomposition of benzil in excess hydrogen iodide produced an excess in gm.-atoms of iodine over moles of carbon monoxide which would not be expected from the mechanism

$$PhCOCOPh \rightarrow 2PhCO- \xrightarrow{(rapid)} 2Ph- + 2CO$$

$$Ph- + HI \rightarrow PhH + I$$

$$I + I + M \rightarrow I_2$$

Since benzaldehyde was found only in traces, the reaction of benzoyl radicals with hydrogen iodide was possibly slight.

For the results of a series of experiments at varying hydrogen iodide partial pressure a linear plot was obtained for a graph of moles iodine produced against partial pressure of hydrogen iodide, which suggested the possible involvement of the hydrogen iodide in a second order reaction with the benzil.

Desoxybenzoin: Decomposition in excess Toluene and in excess Hydrogen Iodide.

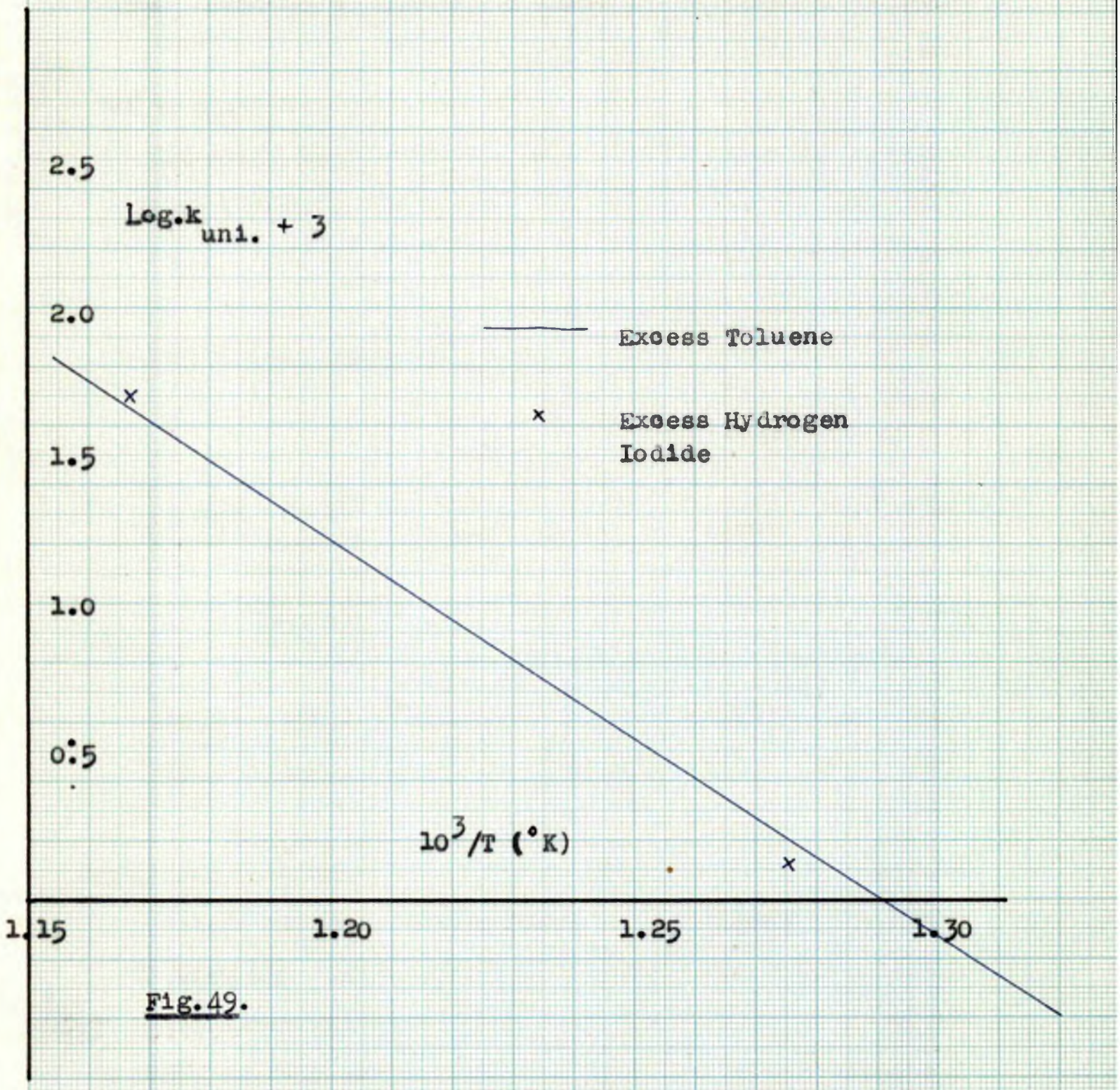


Fig.49.

Examination of the involatile products of the decompositions showed extensive reduction of the benzil to a variety of products. Even the aromatic rings were probably attacked.

In view of the complexity of the reactions, measurement of the amount of iodine produced would be of little kinetic value, and hydrogen iodide would not be a suitable radical acceptor for the benzil decomposition.

Experiments with deoxybenzoin.

Two decompositions of deoxybenzoin in excess hydrogen iodide were performed to test the effect.

TABLE 38

Expt.	Temp. (°C)	Contact time (secs)	gm.atoms iodine	moles carbon monoxide	$\log_{10}k$ in terms of carbon monoxide produced	$10^3/T$ (°K)
164	511	0.76	-	1.20×10^{-6}	$\bar{3}.118$	1.276
165	584	0.59	6.8×10^{-6}	9.30×10^{-6}	$\bar{2}.699$	1.167

When plotted on the same graph as the earlier temperature coefficient data for the decomposition of benzil in excess toluene, shown opposite, these points fell near to the same line. The yield of iodine was so small that it could not be accurately estimated by difference from the background of iodine from the hydrogen iodide at this higher temperature.

Apparently, deoxybenzoin is not attacked by hydrogen iodide in the same way as benzil.

Because of the difficulty of measuring the yield of iodine, the method was not suitable for checking the results of the experiments for decomposition of deoxybenzoin in sealed tubes. Again, little evidence for benzaldehyde was found in the products of these experiments.

Benzophenone decomposition.

84

Clark and Pritchard put forward an explanation for high A factors in the decompositions of some ketones as being the result of simultaneous decomposition of the ketones by several modes. As well as calculations for benzil on the basis of Jaquiss' results, they quoted results for benzophenone. This should have the possibility of decomposition by two modes:

$$PhCOPh = PhCO\cdot + Ph\cdot$$

$$PhCOPh = Ph\cdot + CO + Ph\cdot$$

and a study of its decomposition might throw some light on the applicability of Clark and Pritchard's explanation to the benzil decomposition.

Several decompositions of benzophenone were carried out to see if the results for this apparatus agreed with those of Clark and Pritchard. The same apparatus was used as for the benzil and deoxybenzoin decompositions, and a ten times excess in partial pressure of toluene over benzophenone was present during the reactions.

The benzophenone was obtained from British Drug Houses, Ltd., and was purified to constant and sharp melting point by repeated recrystallisation from ethanol.

Procedure.

The benzophenone and excess toluene were injected just as for the experiments with benzil in excess toluene.

At the high furnace temperature required for the benzophenone

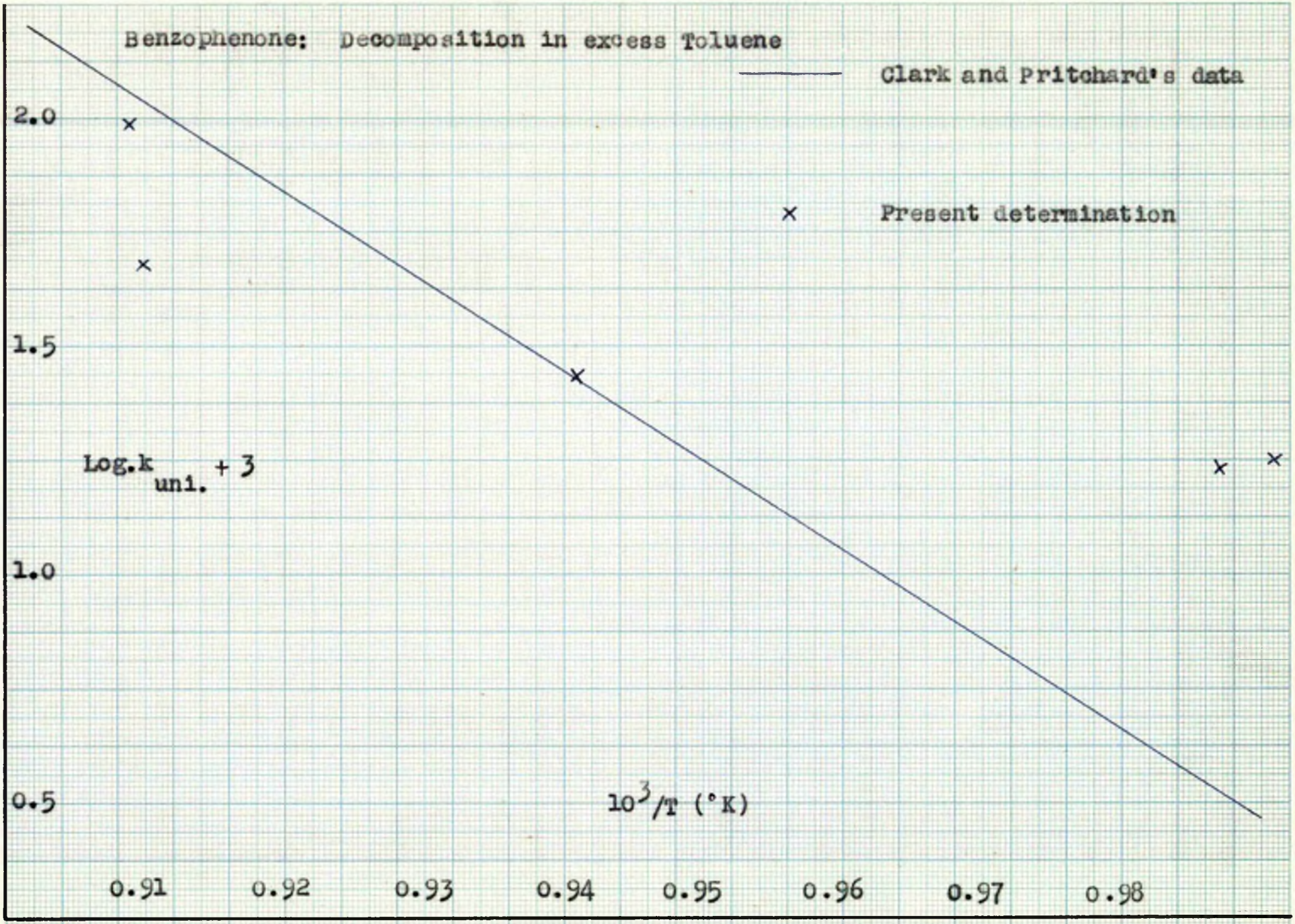

Benzophenone: Decomposition in excess Toluene
Clark and Pritchard's data
Present determination
2.0
1.5
1.0
0.5
Log.k uni. + 3
10³/T (°K)
0.91
0.92
0.93
0.94
0.95
0.96
0.97
0.98

Fig.50.

pyrolysis it was noted that the toluene itself decomposed to give appreciable amounts of gaseous product. This was presumably largely a mixture of methane and hydrogen, and passage over the hot cupric oxide furnace and over liquid oxygen would leave methane. Before each experiment, a blank run with toluene alone was carried out, and the amount of gaseous product subtracted from the total gas for an experiment. A unimolecular rate constant was calculated on the assumption that the remainder of the gaseous product was carbon monoxide, and that the decomposition mechanism was:

$$PhCOEt \rightarrow PhCO\text{-} + Et\text{-}$$

followed by $$PhCO\text{-} \xrightarrow[\text{(rapid)}]{} Ph\text{-} + CO$$

The results are tabulated below.

TABLE 36

Expt.	Temperature °C	Contact Time (secs)	Pressure benzophenone (mm)	$P_{toluene}$ (mm)	$\log_{10}\frac{a}{a-x}$	$10^5/T(°K)$
166	738	0.444	0.080	0.975	1.005	0.991
167	740	0.445	0.005	0.86	0.000	0.987
168	789	0.455	0.007	0.89	1.100	0.941
169	827	0.416	0.070	0.90	1.745	0.900
170	826	0.437	0.007	0.89	1.495	0.910

On the Arrhenius plot opposite, the points from these data are compared with the line from Clark and Pritchard's reported data of temperature

dependence $k = 10^{16.2} e^{-87.5/RT}$. At the highest temperature used, the toluene blank correction amounts to about half the total gaseous product from a reaction, and the points obtained from the difference are not far from Clark and Pritchards' data. At the lowest temperatures used, the toluene blank correction is still about a third of the total yield of gaseous product in an experiment, and the resultant points are far from Clark and Pritchards' data. Repeat experiments confirmed the positions of these points.

The present data was determined using 0.1 mm. benzophenone in about 1 mm pressure of toluene, but Clark and Pritchard used 15 mm. toluene for the same partial pressure (0.1 mm) of benzophenone. At their highest quoted temperature (about 800°C) the gaseous product from the toluene blank must have been very much in excess of the net gaseous product for an experiment. The graph shown by Clark and Pritchard has 11 points covering a temperature range of only 61 degrees, and considering this and the extent of the toluene decomposition and subsequent uncertainty in the measurement of the net amount of gaseous product, their values of A and E must be necessarily approximate.

The involatile products of experiment 170 were dissolved in carbon tetrachloride and examined using the infra-red spectrometer. An absorption band for the carbonyl group of fluorenone was shown quite distinctly, although the percentage decomposition to carbon monoxide for that experiment was only 1.2 and there was a large excess of toluene over benzophenone present. This suggests that the mechanism for the

decomposition is more complicated than was assumed, and much more careful examination of the products would be required before a full mechanism could be set down. Without such a full mechanism involving all the products, A or E values could not be assigned to any particular reaction step.

DISCUSSION.

For reasons of continuity some discussion of experimental results has been given at several points of the earlier part of the thesis, and it is now desirable to summarise the main findings of the work in relation to the general aims of the investigation.

As emphasised in the account of the kinetic method of bond dissociation energy determination, and in the description of the apparatus, it was considered at the outset of the work that some improvements on the general techniques in this field would have to be made in order to obtain an adequate establishment of the kinetic order. Some published work in this field has not paid sufficient care to this matter. The separate injection systems for reactants and radical acceptors which have been described, together with accurate control of flow rates and temperature, have permitted independent variation of the factors necessary to establish kinetic order and appear to be a decided improvement on some current practice.

It is apparent from some earlier work with the toluene carrier technique that if the value of the improved kinetic methods is to be realised, there is a need to examine the products and stoichiometry of radical reactions with greater care. In the present work a variety of physical techniques have been applied, and the results detailed in earlier sections will now be considered together with the

kinetic data.

(a) Benzil decomposition in a flow system.

The investigation of the pyrolysis of benzil without the presence of a radical acceptor has been shown here to be unsuitable for detailed study for the purpose of bond dissociation energy determination.

Throughout this work the tentative hypothesis that the initial decomposition of a benzil molecule yields two PhCO- radicals was a working guide and while most of the quantitative data were on rates of carbon monoxide production, another interest was in the other possible fates of these radicals. From this latter point of view the demonstration by chromatography, ultra-violet and infra-red spectrophotometry of the production of other carbonyl-containing products such as fluorenone and benzophenone did not suggest a simple reaction scheme, and indicated that the carbon monoxide production rates would not give directly the rates of formation of PhCO- radicals. Another feature of the decomposition under these conditions was a "seasoning" of the reaction furnace which was accompanied by some carbon deposition on the walls, and an increase in the initial rate of decomposition.

It was not unexpected that simple kinetic behaviour could not be observed in the pyrolysis of benzil without radical acceptors. The reactivity of phenyl radicals is well known, and the use of toluene as a radical acceptor followed.

It was shown that the use of toluene altered the reaction

behaviour in several ways. It caused a decrease in the rate of carbon monoxide production and as the proportion of toluene was increased, the rate did not fall below about a half of the rate for the reaction without toluene. In the region of minimum rate the presence of fluorenone or benzophenone in the products could not be detected if the (toluene / initial benzil) molar ratio was about five or greater, and the decomposition was restricted to about 5%. Moreover, the slight carbon coating on the furnace wall was not formed.

These conditions, which seemed more appropriate to the determination of quantitative kinetic data, were adopted for the subsequent work.

As far as the stoichiometry was concerned the anticipation that the reaction

$$PhCO- = Ph- + CO$$

would be followed by

$$Ph- + PhCH_3 = PhH + PhCH_2-$$

and give a (benzene / carbon monoxide) molar ratio of unity was approached under the conditions specified above. (The dibenzyl produced was identified, but not estimated).

With the indicated minimum excess of toluene it was shown that the percentage decomposition of benzil in a fixed reaction time was practically independent of its partial pressure over a nine-fold range of variation of the latter. (0.5 mm.- 4.5 mm. Fig. 19). The technical limitations of the flow system prevented a check over a wider range of pressure but this range is greater than that in many

researches using this general technique.

A study of the variation of carbon monoxide production with reaction time showed that a linear relationship holds over a four-fold variation in time. Taking this result in conjunction with the effect of variation in concentration it was evident that with the stated (reactant / toluene) proportions the reaction was first order as assessed from carbon monoxide production.

A reasonable conclusion was that the facts could be explained by an overall mechanism:

$$PhCOCOPh = 2\ PhCO- \qquad (1)$$

$$2PhCO- = 2\ Ph- + 2CO \qquad (2)$$

$$2Ph- + 2PhCH_3 = 2\ PhH + 2\ PhCH_2- \qquad (3)$$

$$2PhCH_2- = PhCH_2CH_2Ph \qquad (4)$$

The experimental work was directed into attempting to find within rough limits where this simple reaction scheme applied.

It has already been suggested that in the absence of toluene the fate of the phenyl radical was not established and somewhat similar conditions have to be considered when the percentage decomposition is high in relation to the amount of toluene present and reaction (3) could not be fully effective. In these latter circumstances diphenyl, benzophenone and fluorenone were found in the products, as well as diphenylmethane or monomethyl diphenyl. It is possible to account for these by radical - radical combinations such as:

$$2Ph- = Ph\text{-}Ph \qquad (a)$$

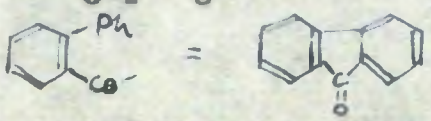
$$Ph- + PhCO- = PhCOPh \qquad (b)$$

$$Ph\cdot + PhCH_2\cdot = PhCH_2Ph \qquad (c)$$

and radical addition reactions such as

$$Ph\cdot + PhCH_3 = Ph\,C_6H_4\,CH_3 + H \qquad (d)$$

$$Ph\cdot + PhCO\cdot = \qquad (e)$$



The kinetic consequences of these reactions would be likely to be marked in the case of (b) and (c) where PhCO· radicals are removed. The experimental work did, in fact, show a fall-off in the rate of carbon monoxide production under the conditions where decompositions were raised from 5 to 65%. Moreover, the (benzene / carbon monoxide) molar ratio decreased to less than 0.5 since reaction (3) was no longer effective.

Evidence of radical addition reactions taking place in solution are plentiful.[77] Though the work of Ingold and Lossing,[35] mentioned in the introduction, suggests that the most likely reactions of a phenyl radical at high temperatures are hydrogen extraction, dimerisation and decomposition to carbon and hydrogen, experiments by Taylor[78] on the decomposition of benzil at 480°C in the presence of naphthalene and anthracene show that phenyl radicals substitute into these large molecules.

Using the experimental conditions which were found necessary to conform with the simple scheme in reactions (1) to (4), the temperature dependence of first order constants was found to be given by

$\log_{10}k = 15.5 - 62100/4.57T.$

Comparison of Jaquiss' data with the results of the Present Work.

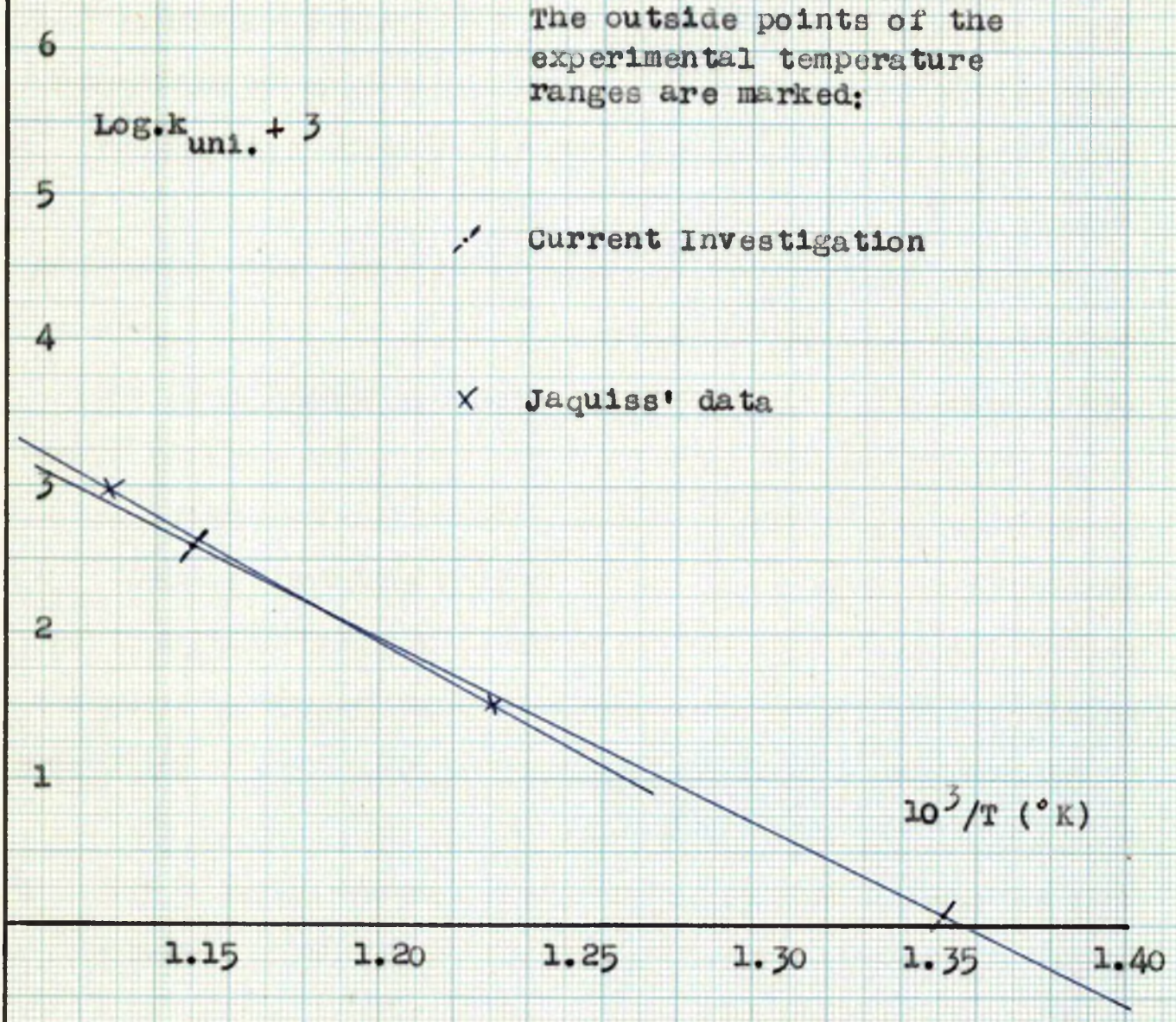


Fig.51.

Before considering the numerical values in this expression and their possible interpretation it is of interest to compare the expression with that for Jaquiss' data[79]: $\log_{10}k = 16.5 - 66600/4.57T$. A graphical illustration (Fig. 51 opposite) of these two expressions shows clearly the greater temperature range covered in the present work.

Jaquiss' experimental arrangement differed from that used here in that the toluene in his technique functioned as the carrier gas as well as being a radical acceptor. A stream of toluene vapour was passed through a sealed U tube containing benzil, the entrained vapour of which was carried forward into the reaction vessel. This arrangement is rather a poor one as far as maintaining a constant partial pressure of benzil is concerned. The exposed surface of the material in the U-tube changes considerably and toluene may dissolve in the substance. Experiments performed by A.M. Mearns[80] in St. Andrews showed that a very non-uniform entrainment of benzyl bromide was obtained with such equipment. Moreover, a general defect of the toluene carrier gas system was evident in Jaquiss' data. Changes which he made in the partial pressure of the toluene resulted in a change in the time of contact, since experimental arrangements to prevent this were not employed.

No mention was made in Jaquiss' thesis of any outgassing procedure for the benzil and no provision for it was evident in his apparatus, yet experiments performed here showed that the decomposition of benzil

was accelerated by the presence of air in the carrier gas stream.

As far as the products were concerned, Jaquiss did not make any detailed examination of the products of the decomposition and did not quote any method for characterising the gases he measured.

In view of these points, and since the temperature range of Jaquiss' experiments was only 75 degrees as compared with 150 degrees for the present work, the results of the present work are assumed to be superior.

(b) Decomposition of deoxybenzoin in a flow system.

The working basis of this study was the anticipation that deoxybenzoin could pyrolyse at its weakest link, the central C-C bond, yielding a benzoyl and a benzyl radical. Since both these radicals were present under very similar physical conditions in the benzil pyrolysis, some of their reactions will be expected to be the same here. For example, it is reasonable to assume a rapid decomposition of the benzoyl radical

$$PhCO\cdot \rightarrow Ph\cdot + CO$$

followed by a removal of phenyl radicals in the presence of toluene by the reaction

$$Ph\cdot + PhCH_3 \rightarrow PhH + PhCH_2\cdot$$

The pyrolysis of deoxybenzoin without an added radical acceptor was again not suitable for kinetic study. The measurement of the rate of carbon monoxide production could not be regarded as a measure

of the rate of PhCO- production since some benzophenone and fluorenone were found in the products even when the decomposition was less than five per cent. The formation of these products could be explained on the basis of radical - radical combinations:

$$Ph\cdot + PhCO \cdot = PhCOPh \qquad (a)$$

or by addition of phenyl radicals to the parent compound:

$$Ph\cdot + PhCOCH_2Ph = PhCOPh + PhCH_2\cdot \qquad (b)$$

When toluene was added as a reaction partner there was no noticeable effect on the rate of production of carbon monoxide when using 4% decomposition, and this suggested that the benzophenone was formed by a reaction of type (b) which would not affect appreciably the rate of PhCO- production and would be favoured by the relatively high concentration of deoxybenzoin.

For benzil, reduction in the proportion of toluene caused an increase in the rate of carbon monoxide production which would be explained by the occurrence of a reaction of type (c)

$$PhCOCOPh + Ph\cdot = PhCOPh + PhCO\cdot \qquad (c)$$

$$PhCO\cdot = Ph\cdot + CO$$

etc. and the initiation of short chain reactions.

Blacet and Bell [81] followed a similar inversion reaction to (b) and (c) in the photolysis of diacetyl vapour over the temperature range 100 - 200°C.

$$CH_3\cdot + CH_3COCOCH_3 = CH_3COCH_3 + CH_3CO\cdot$$

Their determination of the temperature dependence of the rate constant

for this reaction suggests that only a small activation energy is involved.

($\log k = 10.7 - 3000/4.57T$) (k in $mole^{-1}$ cc. sec^{-1})

Although the products of the inversion reactions (b) and (c) could not be distinguished from those of the radical - radical combination reaction (a), the inversion reaction will be favoured on a collision frequency basis in view of the small expected stationary concentration of PhCO- radicals.

For desoxybenzoin, a (toluene / desoxybenzoin) molar ratio of 10 allowed the percentage decomposition to be carried to 15.1% without the formation of benzophenone or fluorenone and these conditions were adopted for the subsequent kinetic work. In the study of the pyrolysis of desoxybenzoin under these conditions the percentage decomposition as assessed by carbon monoxide production rate was independent of the partial pressure of desoxybenzoin over a tenfold range of the latter (0.015 mm. - 0.17 mm. Fig. 35), and a linear relationship was found to hold between percentage decomposition and contact time over a seven-fold variation of the latter (Fig. 37).

These facts suggest a mechanism

$$PhCOCH_2Ph = PhCO- + PhCH_2-$$

$$PhCO = Ph- + CO \quad [\text{rapid}]$$

From the benzil study, the phenyl radical would be expected to be removed by

$$Ph\cdot + PhCH_3 = PhH + PhCH_2\cdot$$

and then, $$2PhCH_2\cdot = PhCH_2CH_2Ph$$

Under the same conditions of (toluene / deoxybenzoin) molar ratio the temperature dependence of first order constants as deduced from carbon monoxide production was found to fit the expression $\log_{10}k = 14.1 - (59000/4.57T)$, over a temperature range of 108 degrees, and tests showed that the decomposition was homogeneous.

(c) Reactions in a static system.

Although the temperature ranges of these two kinetic studies are greater than for some of the reported work using this general method, attempts were made to extend the work to lower temperatures by carrying out reactions in static reaction bulbs. Despite the use of (toluene / reactant) molar ratios greatly in excess of 10, the decompositions were complicated by the production of benzophenone, fluorenone, and other carbonyl-containing products.

At the higher partial pressures of reactant which were necessary to obtain measurable amounts of carbon monoxide under static system conditions, it is quite likely that even this proportion of toluene was not sufficient to prevent the same kind of radical - radical combinations and additions as occurred for high percentage decomposition of benzil in the flow system.

(d) Reactions with hydrogen iodide.

Study of the decomposition of alkyl iodides in the presence of hydrogen iodide by Butlerov[70] and, more recently, by Ogg,[71] showed that the decomposition of the iodide

$$RI = R\cdot + I \qquad (1)$$

may be followed by removal of the radical R·, and the production of an atom of iodine.

$$R\cdot + HI = RH + I \qquad (2)$$

Since the decomposition of hydrogen iodide itself is bimolecular

$$2\,HI = H_2 + I_2 \qquad (3)$$

even though it requires an activation energy of only 44 k cal/mole, under conditions of low pressure and moderate temperature the rate of decomposition is low. Hence, it might be expected that the decomposition at low pressure of a substance in the presence of excess hydrogen iodide would give radicals which reacted as in reaction (2), and the decomposition could be followed by the rate of production of iodine.

Experiments with benzil showed that products were formed which would agree with a mechanism of the type:

$$PhCOCOPh = 2PhCO\cdot$$

$$PhCO\cdot + HI = PhCHO + I \quad \text{(to small extent)}$$

$$PhCO\cdot = Ph\cdot + CO$$

$$Ph\cdot + HI = PhH + I$$

$$2I = I_2$$

but the total reaction was more complex, since the benzil was apparently attacked by the hydrogen iodide to give reduced products. The precise amount of this extensive reduction was not known but the iodine so formed made measurement of rates of iodine production an insecure basis for kinetic work.

Deoxybenzoin was not apparently attacked in this way, and under conditions of low pressure, its decomposition might have been studied by measurement of the rates of iodine production, but the extent of the hydrogen iodide decomposition at the temperatures of the deoxybenzoin study (515 - 615 °C) set an upper limit for the convenient application of the method when using pressures of hydrogen iodide of about 0.8 mm.

The method has been applied with some success at St. Andrews by Downs and Gow[72,25], in the study of the pyrolyses of iodides at temperatures about 100 degrees lower.

TABLE 56

Compound	E (k cal/mole)	A (sec^{-1})
Diethylmercury	42.5	1×10^{14}
Phenylmercury chloride	59	1×10^{15}
Phenylmercury bromide	63	1×10^{14}
Diphenylmercury	68	1×10^{16}
Acetophenone	77.6	5.1×10^{15}
Benzophenone	87.5	1.6×10^{16}
Dibenzyl ketone	71.8	1.8×10^{17}
Acetone	70.9	1.4×10^{14}
Trifluoroacetone	67.8	0.5×10^{14}
Trifluoroacetophenone	75.8	1.8×10^{15}

Magnitude of frequency factor and mechanism.

In 1928, Polanyi and Wigner[82] put forward a suggestion that the normal frequency factor in the Arrhenius equation for bond dissociation reactions is $10^{15} sec^{-1}$. They based the suggestion on theoretical arguments and on the results of several decomposition reactions, many of which proved later to be complex.

Steacie[46] points out that most frequency factors do fall within the range 10^{12} to $10^{14} sec^{-1}$ and that, in the absence of a better value, 10^{13} has often been assumed. The A factors for the currently studied decompositions fall outside this "normal" range.

In 1956, Carter, Chappel and Warhurst[83] quoted some activation energy and frequency factor data for mercury alkyl compounds and suggested a grouping into "high" and "normal" frequency factors. In the same year Clark and Pritchard[84] drew attention to some keto compounds where the kinetics of decomposition showed some similar features. Some of the data for these compounds is quoted in table 36. opposite.

These decompositions were carried out in the gas phase but a recent study of the decomposition of mercury dibenzyl in the inert solvent iso-octane[86] gave $k\ (sec^{-1}) = 10^{16.25} \exp(-38,800/RT)$. Also Ziegler and collaborators[87] carried out a series of studies of the rate of dissociation of polysubstituted ethanes and found results as shown below:

TABLE 37

Compound	E (k cal)	A (sec^{-1})
Tetraphenyl dimethylethane	30.0	1.9×10^{16}
" diethylethane	27.2	4.4×10^{17}
" di-n-propylethane	26.7	9.5×10^{17}
" di-n-amylethane	26.6	7.1×10^{17}
" di-isopropylethane	25.0	4.2×10^{14}
Di-n-propyl dixanthyl	30.0	1.8×10^{15}

These latter studies by Ziegler et alia are clear cases of initial dissociation into radicals by single bond fission and so differ from the mercury alkyl and aryl compounds and the ketones, where the products require the eventual rupture of two bonds.

Before discussing the theories used to explain such "high" experimental A factors, it is interesting to examine an interrelation of the A factors for the forward and back reactions of the process $X_2 \rightleftharpoons 2X$.

It is well known that the temperature independent factors for the forward and reverse reactions of a chemical change are related to the entropy change of the process. Thus for the reaction

$$L + M \rightleftharpoons P + Q \qquad (1)$$

$$K_c = \frac{k_F}{k_R} = \frac{A_F \; e^{-E_F/RT}}{A_R \; e^{-E_R/RT}}$$

where the subscripts F and R refer to the forward and reverse reactions and K_c is the equilibrium constant in concentration units.

$$\therefore \ln K_c = \ln A_F/A_R - (E_F - E_R)/RT.$$

Now $\ln K_p = \frac{-\Delta F^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$,

and if the reactants and products are treated as perfect gases

$$K_p = K_c (RT)^{\Delta n}$$

where Δn = (no. of moles product - no. of moles reactant)

and R is in l. atm. $mole^{-1}$.

$$\therefore \ln K_p = \ln K_c - \Delta n \ln RT$$

$$\therefore \ln K_c = \ln K_p - \Delta n \ln RT = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} - \Delta n \ln RT$$

$$\text{and} = \ln A_F/A_R - (E_F - E_R)/RT.$$

If we equate $\frac{\Delta H^\circ}{RT} = (E_F - E_R)/RT$

$$\text{then } \ln (A_F/A_R) = \frac{\Delta S^\circ}{R} - \Delta n \ln RT$$

In this expression ; in $\frac{\Delta S^\circ}{R}$, S° is in cals. $deg^{-1} mole^{-1}$

, R in calories . $mole^{-1}$

in $\Delta n \ln RT$, R is in l-atmospheres. $mole^{-1}$

For a dissociation $X_2 \rightleftharpoons 2X$ at 300°K.

$$\Delta n \ln RT = 1 \times 2.303 \log 0.082 \times 300$$

$$= \underline{5.2}$$

$$\ln (AF/A_R) = \frac{\Delta S^\circ}{R} - \Delta n \ln RT$$

$$\log (AF/A_R) = \frac{\Delta S^\circ}{4.97} - 5.2$$

To determine ΔS° for $X_2 \rightleftharpoons 2X$, estimations must be made of the standard entropies of the molecule X_2 and the radicals X. If the association of the radicals X is assumed to be without activation energy, and if the A_R factor for the process is assumed to be of the usual bimolecular magnitude, then by using the ΔS° value for the dissociation of X_2 an "expected" maximum value for the A_P factor for the dissociation can be calculated. If this is as large as the experimental value for A_P, then the assumed rate of radical recombination is reasonable. It would always be possible for lower values of A_P and A_R to be obtained since only their ratio features in the above expression.

The estimation of the standard entropies of benzil and the benzoyl radical is difficult because of the small amount of experimental data available for compounds of this type. For a molecule such as benzil the main contributions to the entropy might come from (a) translation of the whole molecule; (b) rotation of (i) the whole molecule considered as a rigid structure; (ii) groups within the molecule. From calculations of these contributions[88] it is known that the vibrational contribution to the entropy is relatively small at moderate temperatures and, to a first approximation, can be neglected.

The benzoyl radicals from the unimolecular split of a benzil molecule would each possess entropy divisible into similar components. When compared with the initial state the products have extra degrees of freedom of translation and rotation arising from the increase in

the number of particles, but there would be the loss of the internal rotation round the central bond in benzil.

Before attempting a calculation of the entropy increase for the dissociation of benzil, it is interesting to look at other reactions for which ΔS° data exists for molecules and the dissociated products.

e.g. (a)[89] Iodine has approximately the same molecular weight as benzil

$$I_2\,(g) \rightleftharpoons 2\,I\,(g)$$

ΔS° = (2x45.18) - 62.28 = 28.08 eu.

This system is really too simple for comparison, the translational entropy term being the main contributor.

(b) N_2O_4 has a smaller mass but larger bulk than iodine, and for the dissociation $N_2O_4 \rightleftharpoons 2\,NO_2$

Shepp and Bauer[90] quote ΔS° = (2x57.47) - 72.73 = 42.21 eu.

Shepp and Bauer also made entropy calculations for the dissociation reactions of a number of boron compounds.

e.g. (c) $B_2H_6 \rightleftharpoons 2BH_3$

ΔS° = 2(44.91) - 35.60

= 34.22 eu.

(d) $Me_3N{:}BH_3$ = NMe_3 + BH_3

ΔS° = 37.80 eu.

Though the systems considered here are simpler than that for benzil, from these examples, a very rough anticipation of the order of ΔS° to be expected for the benzil dissociation might be 30 - 40 eu.

The methods of estimating standard entropies may be drawn roughly into two groups.

(1) Calculations of the translational and rotational etc., components for the standard entropies of molecules and radicals, using statistical formulae involving the masses, moments of inertia etc., of the particles.

(2) Empirical methods of assessing thermodynamic properties based on the idea of group contributions. These methods are outlined in greater detail in the appendix and are used there for calculating the following data.

(1) For the benzil dissociation

$$\Delta S^{\circ}_{tr.} = (2 \times 39.79) - 41.7$$

$$= \underline{37.88 \text{ eu.}}$$

and $\Delta S^{\circ}_{rot^{n}}$ (on the basis of rigid rotators)

$$= (2 \times 27.89) - 55 = \underline{22.78 \text{ eu.}}$$

i.e. $\Delta S^{\circ}_{tr. + rot^{n}} = \underline{60 \text{ eu.}}$

The actual value must be less than this due to internal rotations possessed by the molecule and not by the radicals. The magnitude of the entropy increment due to internal rotation is not likely to be as large as that due to rotation of the whole molecule, so that ΔS° is <60 eu and probably at least 30 - 40 eu.

(2) More faith could be placed on the estimations of the entropies

of compounds of the type Ph - C - C - Ph (in some of which conjugation effects are likely) if more experimental entropy data were available for compounds of this type. However, for the dissociation of dibenzyl

$$PhCH_2CH_2Ph = 2PhCH_2\cdot$$

it is shown in the appendix that empirical estimates give

$$\Delta S^\circ = 2\,S^\circ_{PhCH_2\cdot} - S^\circ_{PhCH_2CH_2Ph}$$

$$= 2\,(76.4) - 120 = \underline{32.8 \text{ eu}}.$$

If we assume that combination of two benzoyl radicals occurs at the collision frequency, then the A_R factor for the combination would be approximately 10^{11} l. mole^{-1}sec^{-1}.

$$\text{Now } \log A_P = \log A_R + \frac{\Delta S^\circ}{4.57} - 3.2$$

$$= 11 + \frac{32.8}{4.57} - 3.2$$

$$= \underline{15.0}$$

Davidson[91] found the experimental A factor for the dissociation of dibenzyl as $10^{14.9}$, in close agreement with the above value, so it is evidently possible to correlate the "high" experimental A_P factor with an A_R factor of conventional magnitude.

From the foregoing discussion, and the estimates in the appendix, it seems possible that the increase in standard entropy for the dissociation of benzil should be about 30 - 40 eu. Also, similar magnitudes of ΔS° might be anticipated for the dissociations

$$PhCOCOPh = 2\,PhCO\cdot$$

$$PhCH_2CH_2Ph = 2\,PhCH_2\cdot$$

in view of the similarity of the processes.

Thus, similar reasoning and assumptions as for dibenzyl, lead to an "expected" A_p value for the benzil dissociation of about 10^{15} sec^{-1}. This is in reasonable agreement with the experimental value of $10^{15.5}$.

While the above considerations show that high A_p values are possible when there is a dissociation into two large fragments and A_R has a "normal" value, they do not provide an interpretable rate equation for, or mechanistic interpretation of, the dissociation process.

In 1936, Pritchard[92] put forward an explanation for the high frequency factors found in the pyrolysis of the group of mercury alkyls by the toluene carrier technique. He suggested that simultaneous decomposition by two modes was possible because of the very small amount of energy required to break the second alkyl link in reaction (16)

$$HgR_2 = HgR + R \qquad (1a)$$

followed by

$$HgR = Hg + R \qquad (1b)$$

or

$$HgR_2 = Hg + 2R \qquad (2)$$

The general equation for the decomposition rate was written:

$$k = \lambda \cdot \exp(-E/RT) \cdot \sum_{r=0}^{S-1} \frac{1}{r!} (E/RT)^r$$

where λ has the dimensions of frequency and S is the number of classical internal vibrations contributing to the reaction co-ordinate.

For a particular compound, a value of S was chosen to give a calculated rate as near as possible to the experimental rate at a temperature about in the middle of the experimental range. The choice of was arbitrarily made to produce as good agreement as possible with experimental rates for the group of dialkyls. When the decomposition rates were calculated for temperatures over a 100 degree range, and log k against $10^3/T$ plotted, the values of A and E deduced from the line agreed well with the experimental values.

This explanation was extended to a group of ketones, including benzil, in a further paper by Clark and Pritchard.[84] For monoketones, the two modes of decomposition envisaged were

$$R_2CO = RCO + R \qquad (1a)$$

$$RCO = R + CO \qquad (1b)$$

and $$R_2CO = 2R + CO \qquad (2)$$

In this case, the activation energy for process (1b) is higher than for the equivalent mercury alkyl decomposition.

Amongst the compounds for which data was quoted was benzophenone, and since a supply of this compound was readily available, a few experiments were carried out to see if the quoted results could be reproduced. The results of these experiments are tabulated in an earlier section and from them, there seems to be some doubt about the validity of the results quoted by Clark and Pritchard for benzophenone.

Carboxyl containing compounds, occurring in the involatile products of benzophenone decomposition, would need to be analysed

for CO content before an accurate assessment of the initial decomposition could be made. No method of characterisation of the gaseous products was mentioned by Clark and Pritchard, though this would be necessary in view of the great extent of decomposition of the excess toluene present. These observations suggest that a closer inspection of the products would be necessary before a temperature coefficient for the rate of the benzophenone decomposition could be determined.

Pritchard's explanation has been reviewed by Johnston[93] in the light of more recent rate theory.

Szwarc and Herk[94] recently considered the decomposition of substances which yield thermochemically unstable radicals which then decompose exothermally. For a molecule ABC dissociating at its weakest bond to give an unstable radical BC:

$$ABC = A + BC$$

followed by $$BC = B + C + \text{Kcals.}$$

Szwarc and Herk visualised the dissociation of the BC bond beginning before that of the AB bond was complete. In this way, the measured activation energy may be intermediate between that of the bond AB alone and that for the simultaneous fracture of both the AB and BC bonds. As the radical BC becomes more stable, and its decomposition becomes more endothermic, there would be a smaller chance of this occurring simultaneously with the primary split.

This simultaneous decomposition at two bonds may occur with the mercury alkyls, where the activation energy for the decomposition of

the HgR radical is < 10 B cal. For the decomposition of compounds to give the benzoyl radical, where the activation energy for the decomposition of the latter may be ~ 27 k cals (as estimated in the introduction), this simultaneous decomposition seems less likely, and the applicability of the Pritchard type working less convincing.

The explanations just given involve ideas based on the simultaneous rupture of more than one bond. In cases where only one bond is broken it would be necessary to use the equation

$$k = \lambda \exp(-E/RT) \sum_{r=0}^{S-1} \frac{1}{r!} \left(\frac{E}{RT}\right)^r$$

in the normal way to indicate the chance of a molecule aquiring the energy E from 2r square terms.

If the initial step in the dissociations studied is assumed to be the split of the central C-C bond only, and if the experimental activation energies are assumed to be equal to the respective dissociation energies for the two processes

$$PhCOCOPh = 2PhCO-$$

$$PhCOCH_2Ph = PhCO- + PhCH_2$$

some interesting thermochemical deductions can be made.

Thermochemistry.

(a) Magnitude of the activation energies.

A check on the experimental data for the heats of formation of benzil, desoxybenzoin and dibenzyl, and for the activation energy for their separate dissociations should be afforded by the fact that the heat of the hypothetical reaction

$$PhCH_2CH_2Ph + PhCOCOPh = 2PhCOCH_2Ph$$

should be equal to

$$2D\ (PhCOCH_2Ph) - D\ (PhCOCOPh) - D\ (PhCH_2CH_2Ph).$$

Davidson[91] had determined $D\ (PhCH_2-CH_2Ph) = 60.0$ k cal/mole so the only unknown quantity was $\Delta H_f(PhCOCH_2Ph)$. This was calculated as +6.6 k cal/mole by the method of Anderson, Beyer and Watson.[95] As a check on the method of calculation, the heats of formation were estimated for several compounds for which an experimental value is known.

TABLE 38

Compound	$\Delta H_f^\circ(g)$ Calc^d	$\Delta H_f^\circ(g)$ Exptal.	Reference
Benzophenone	+ 11.8	+ 12.5	96
Benzil	- 21.0	- 21.8	96
Dibenzyl ketone	+ 1.4	+ 1.0	96
Dibenzyl	+ 34.6	+ 29.7	97

On the whole, the method appears to give reasonable agreement with experiment.

Using these heats of formation, for the reaction

$$PhCOCOPh + PhCH_2CH_2Ph = 2\ PhCOCH_2Ph$$

$$\Delta H = 2(6.6) + 29.7 - 21.8 = \underline{5.3 \text{ k cal/mole}}.$$

From the experimental activation energies

$$2D(PhCOCH_2Ph) - D(PhCOCOPh) - D(PhCH_2CH_2Ph)$$

$$= 119.6 - 62.1 - 60.0 = -\underline{3.4 \text{ k cal/mole}}.$$

i.e. there is an accumulated discrepancy of 7.7 k cals between the determinations.

In a survey of methods of calculation of heats of formation Jans[98] finds that Anderson, Dwyer and Watsons' method has a possible error of ± 4 k cals, so the possible error in $2\Delta H_f$ ($PhCOCH_2Ph$) is itself greater than the discrepancy. Taking this and the possible errors for the experimental determinations of D and ΔH_f into consideration, the discrepancy is not unexpectedly great.

The bond dissociation energies for the fission of the central C-C bond of benzil (62.1), desoxybenzoin (59.8) and dibenzyl (60.0) are quite close together, and in this connection some observations on infra-red spectra are of interest.

Rasmussen[99] observes that for benzil, the carboxyl infra-red absorption frequency occurs at 1681 cm^{-1}, which is about the frequency observed for a phenyl-conjugated carboxyl. This suggests that there is little conjugation between the adjacent carboxyl groups.

Kohlrausch and Pongratz[100] quote the Raman-active carboxyl absorption frequency for benzil as 1685 cm^{-1} and Rasmussen suggests that the small

difference between this frequency and that of the infra-red band also suggests little interaction between the two carbonyls, and hence a relatively weak central C-C bond and low degree of conjugation.

An interesting contrast can be made with biacetyl, for which the infra-red absorption frequency is 1718 cm^{-1}, and the Raman-active carbonyl frequency 1735 cm^{-1} i.e. a greater difference than for benzil. Walters,[101] using Pitzer's values,[102] notes that in the decomposition of biacetyl, the contribution to the entropy of activation resulting from free rotation of the CO - CO bond in the activated complex might be appreciable. From dipole moment measurements, Zahn[103] has shown that there is restriction to rotation about the CO - CO bond in diacetyl.

Spectroscopic work on glyoxal,[104] and electron diffraction work on biacetyl,[105] have shown them to be trans. By analogy, and because of the phenyl group repulsion, benzil is probably trans.

These indications of little interaction between the adjacent carbonyl groups in benzil are in agreement with the similarity between the strengths of the central carbon - carbon bonds of benzil (present work) and dibenzyl (Davidson).[91]

(b) Heats of formation of radicals deduced from the present work.

(i) ΔH_f (PhCO-)

From the activation energy for the benzil decomposition

$$PhCOCOPh = 2PhCO- - 62.1 \text{ k.cals}$$

since ΔH_f°(benzil) = -21.8 k.cal.

$$\Delta H_f^\circ(PhCO-) = \tfrac{1}{2}\left[D(PhCOCOPh) + \Delta H_f^\circ(PhCOCOPh)\right]$$

$$= \tfrac{1}{2}(62.1 - 21.8) = \underline{20.1 \text{ k.cal.}}$$

(11) $\underline{\Delta H_f^\circ (PhCH_2-)}$

From the reaction

$$PhCOCH_2Ph = PhCO- + PhCH_2- - 59.8 \text{ k.cal.}$$

$$\Delta H_f^\circ(PhCH_2-) = D(PhCOCH_2Ph) - \Delta H_f^\circ (PhCO-) + \Delta H_f^\circ(PhCOCH_2Ph)$$

$$= 59.8 - 20.1 + 6.6 = \underline{46.3 \text{ k.cal.}}$$

It is convenient to summarise here previous experimental work leading to these heats of formation, some of which has been described in detail earlier in the thesis.

(i) Benzoyl radical.

Benzoyl bromide was pyrolysed by the toluene carrier technique by Ladacki, Leigh and Szwarc[40] and the products were subjected to a complete mass balance. The heat of formation of the benzoyl radical was deduced as 15.6 k.cal.

Szwarc and Taylor[41] later pyrolysed benzoyl chloride by the same technique and obtained a value for the benzoyl radical heat of formation of 15.7 k cal. This agreement is apparently very good, but no explanation was given for the difference in A factors for the two reactions by a factor of 50.

As mentioned earlier, Jaquiss and Szwarc pyrolysed benzil by the toluene carrier technique but did not publish their results. They determined D(PhCO-COPh) = 66.4 k cals. and ΔH_f(PhCO-) can be deduced from this (using ΔH_f°(benzil) = -21.8 k cal) as 22.5 k cal.

Because of the wider temperature range used, and the more refined experimental technique, the results of the present work on benzil are likely to be more reliable than those of Jaquiss. Similar criticisms about the possibility of the solution of toluene in the reactant and the impossibility of independent variation of the toluene partial pressure and the contact time could be made of the technique used for pyrolysis of the benzoyl halides and of Jaquiss' pyrolysis of benzil.

More work requires to be done to resolve the difference between the determined heats of formation of the benzoyl radical. The values are tabulated below.

TABLE 39

ΔH_f°(PhCO-)	Source	Reference.
15.6	Pyrolysis of PhCOBr. D(PhCOBr)=57.0	40
15.7	Pyrolysis of PhCOCl. D(PhCOCl)=75.6	41
22.5	Pyrolysis of benzil. D(PhCOCOPh)=66.4	79
20.1	Pyrolysis of benzil. D(PhCOCOPh)=63.1	This work.

(ii) Benzyl Radical.

In 1945, Kistiakowsky[18] and van Artsdalen completed some work on the photobromination of toluene, which is outlined in the introductory part of the thesis, and from these studies deduced a value of $\Delta H_f(PhCH_2\text{-})$ (48.4 ± 1.4 k.cals.) Benson and Buss however, have since questioned the simplicity of the assumed mechanism on the ground that the recombination of bromine atoms

$$Br + Br + M = Br_2 + M$$

does not take place as readily as was assumed.

In 1948, Szwarc[7] published a research into the pyrolysis of toluene and, assuming the simple mechanism given in the introduction, deduced a value for $D(PhCH_2\text{-}H)$ = 77.5 k cal/mole. This gives $\Delta H_f(PhCH_2\text{-})$ = 37.8 k cal. More recent work by Blades, Blades and Steacie[24] shows that the mechanism for the toluene decomposition cannot be so simple as Szwarc assumed since the "first order rate constants" vary considerably with contact time and the products are more complex than Szwarc's mechanism would allow. This latter work however, does not establish an alternative mechanism.

In 1950 Szwarc, Ghosh and Sehon[107] pyrolysed bromide by the toluene carrier technique and deduced $D(PhCH_2\text{-}Br)$ = 50.5 k cal. This leads to a value of $\Delta H_f(PhCH_2\text{-})$ = 43.0.

Szwarc claimed support for this value for $D(PhCH_2Br)$ from the facts that $D(PhCH_2\text{-}H) - D(PhCH_2\text{-}Br)$

$$= 77.5 - 50.5$$

$$= 27 \pm 5.3 \text{ k cal.}$$

and that Gellner and Skinner[108], from heats of hydrolysis measurements, had independently determined this difference as 29 ± 3 k cal. However, the determination of $D(PhCH_2\text{-}Br)$ by this method might be liable to the same sort of errors as the determination of $D(PhCH_2\text{-}H)$ by Szwarc, i.e. both $D(PhCH_2\text{-}H)$ and $D(PhCH_2\text{-}Br)$ might be in error in the same sense.

In 1954, Schissler and Stevenson[6] applied the indirect method of electron impact in finding the appearance potential of the $C_7H_7^+$ ion, believed to be the benzyl ion, from the mass spectra of toluene, ethylbenzene, and dibenzyl, and deduced $D(PhCH_2\text{-}H) = 77 \pm 3$ k cal/mole. However, as is outlined in the introduction, Farmer, Henderson, McDowell and Lossing[10] showed that if the appearance potential of the $(C_7H_7^+)$ ion from toluene and the measured ionisation potential of the benzyl radical are combined, $D(PhCH_2\text{-}H)$ can only be deduced as $\geqslant 85$ k cal., and $\Delta H_f\ (PhCH_2^-)$ as $\leqslant 33$ k cal.

In 1956, Alexander[109] completed some work in St. Andrews on the reaction of toluene and iodine. He discovered a side reaction, the decomposition of dibenzyl in the presence of excess hydrogen iodide, where the conditions could be so arranged that the reaction was zero order with respect to hydrogen iodide, and first order with reference to dibenzyl. His experimental results were explained by a reaction scheme as follows:

$$PhCH_2CH_2Ph = 2PhCH_2\cdot$$

$$PhCH_2\cdot + HI = PhCH_3 + I \text{ (rapid)}$$

$$2I = I_2$$

From measurements of the rates of iodine production he deduced that the temperature dependence of the first order rate constants for dibenzyl are given by

$$\log_{10} k = 13.1 - 61000/4.57\ T.$$

In 1957, Davidson[91] completed a study of the initial state of the equilibrium

$$PhCH_2CH_2Ph + PhCD_2CD_2Ph \rightleftharpoons 2PhCH_2CD_2Ph$$

in a static system. He followed the progress of the reaction by mass spectrometer, and measured the rate of appearance of the mass 184 peak ($PhCH_2CD_2Ph^+$ ion). At low pressures the correction for loss of dibenzyl by benzyl attack was small, and allowing for this, Davidson was able to calculate the temperature dependence of the first order rate constants for the dibenzyl dissociation as fitting the expression

$$\log_{10} k = 14.9 - 60,000/4.57\ T.$$

The two latter sets of results, plotted on the same graph, gave two almost parallel Arrhenius plots, with a small step at the junction of 0.6 in log A, and together covered a temperature range of 250°C. In view of the uncertainty of estimation of the exact hot length of the furnace in flow experiments, a step in the combined graph might be expected, and the fact that the two gradients agree so well and cover such a large temperature range is good evidence in favour of an activation energy of 60 -61 k cals. If this value is assumed as the bond dissociation energy for dibenzyl, $\Delta H_f(PhCH_2\text{-})$ is given as 44.9 k cal.

12

The work of Benson and Buss on the equilibrium between bromine and toluene is discussed in the introduction under "Equilibrium methods of bond dissociation energy determination". They deduced a value for $\Delta H_f^{\circ}_{(g)}(PhCH_2\text{-})$ of 44.9, which is identical with Davidsons and Alexanders value.

The last three values, particularly the two determined in St. Andrews, seem to have been deduced from more reliable kinetic measurements than the earlier work, and the value deduced from the present work: $\left[\Delta H_f^{\circ}(PhCH_2\text{-}) = 46.3 \text{ k cal}\right]$ is in good agreement with them.

The values discussed are tabulated below:

TABLE 40

$\Delta H_f^{\circ}(PhCH_2\text{-})$	Source	Reference
48.4	Photobromination of toluene	18
37.8	Pyrolysis of toluene $D(PhCH_2\text{-H})=77.5$	7
45.0	Pyrolysis of benzyl bromide. $D(PhCH_2\text{-Br})=50.5$	107
$\leqslant 55$	Electron bombardment $D(PhCH_2\text{-H}) \geqslant 98$	6,10
44.9	$PhCH_2CH_2Ph + PhCD_2CD_2Ph$ reaction	91
44.9	$PhCH_2CH_2Ph + HI$ reaction	109
44.9	$PhCH_3 + Br_2 \rightleftharpoons PhCH_2Br + HBr$-Equilibrium	12
46.3	This work.	

SUMMARY.

Pyrolysis of benzil.

(1) Benzil was decomposed thermally in a flow system, the extent of the reaction being followed by measurement of the amount of carbon monoxide produced. The products were analysed by ordinary gas analysis, and using a mass-spectrometer and infra-red and ultra-violet spectrometers. The decomposition was complicated by secondary reactions giving carbonyl-containing products and diphenyl.

(2) Decompositions of benzil were carried out in the presence of excess toluene in an attempt to remove phenyl radicals. Under conditions of high conversion of benzil to carbon monoxide similar complicating products were formed as in reactions without toluene, but the attempt was successful at low conversions. Using low percentage decomposition and excess toluene it was shown, by separate variation of the concentration of benzil and toluene and reaction time, that the reaction was first order in benzil and independent of toluene concentration. The dependence of the velocity constant on temperature was given by $\log_{10} k\ (sec^{-1}) = 15.3 - (62{,}100/4.57T)$.

It is considered that the rate determining step is $PhCOCOPh \rightarrow 2\ PhCO$ and that the 62.1 k cals is the central C–C bond dissociation energy.

The benzoyl radicals decompose rapidly to CO and phenyl radicals, the latter being removed by reaction with toluene.

(5) Attempts to extend the temperature range by the use of a static system showed that the reaction was much more complex than in the flow system and produced carbonyl-containing products.

Pyrolysis of deoxybenzoin.

(4) Experiments were carried out in a flow system on the pyrolysis to low percentage decomposition of deoxybenzoin, in the presence of excess toluene. Using similar variations of conditions as for benzil the first order constants are described by

$$\log_{10}k\ (sec^{-1}) = 14.1 - (39000/4.57T)$$

The energy of activation is considered to apply to the process

$$PhCOCH_2Ph = PhCH_2\cdot + PhCO\cdot$$

(5) As with the experiments using benzil, reactions in a static system were complicated by the production of carbonyl-containing products, and one at least of the products seemed to have quite complex aromatic character.

Decompositions with hydrogen iodide as radical acceptor.

(6)(a) Since hydrogen iodide had proved a successful radical acceptor in the pyrolysis of dibenzyl experiments were carried out with benzil in a flow system in which the excess toluene was replaced by excess hydrogen iodide. Small quantities of benzaldehyde were found in the products, which might indicate slight reaction between benzyl radicals and hydrogen iodide, but reduction of the benzil by the hydrogen iodide was extensive and gave complex products.

(b) Although unsuitable as a radical acceptor with benzil

hydrogen iodide did not reduce desoxybenzoin at the temperature of the decomposition of the latter and the yields of carbon monoxide were in agreement with those obtained with toluene. The higher temperatures involved, however, caused considerable decomposition of the hydrogen iodide and for this reason it proved unsuitable as a radical acceptor.

Correlations with other work.

(7) (a) A survey has been given in the introduction of relevant experimental work on benzoyl and benzyl-containing compounds.

(b) The high "A" factors of the decompositions were studied in relation to those of other work and current explanations of them. It is suggested that if the recombination reactions of the radicals involved in the present work have normal temperature independent factors the estimated entropy change for the dissociation may lead to an expectation of high "A" factors.

(c) Making the assumption that the rate of combination of benzoyl radicals is equal to their frequency of collision, the heat of formation of the benzoyl radical has been calculated from this work as 20.1 k cal. This differs from the value of 15.6 k cal. derived from the pyrolysis of the benzoyl halides.

(d) Using the 20.1 k cal. value, a heat of formation of the benzyl radical of 46.5 k cal. has been deduced from the results of the pyrolysis of desoxybenzoin. This is in reasonable agreement with the value of 44.9 k cal. resulting from recent work with dibenzyl.

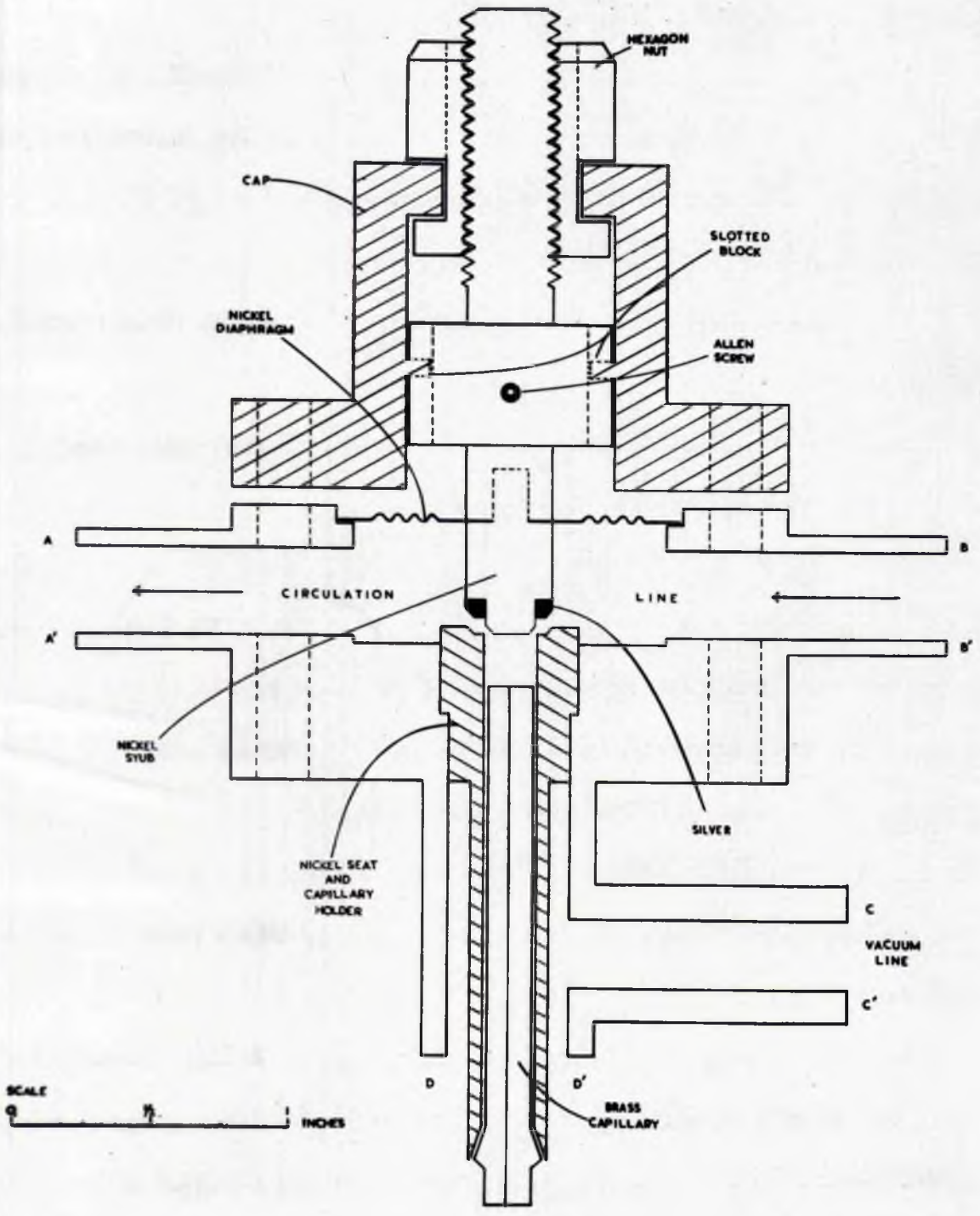


Fig.52. DIAPHRAGM VALVE

APPENDIX 1

The benzil injection valve.

The requirements for this valve were that it should be vacuum-tight, that it should not cause decomposition of the reactants, and that it should withstand prolonged heating to about 250°C. Experiments with valves using brass bellows as the vacuum seal failed on the first count because of the short life of brass when flamed at about 200°C.

Valves using a diaphragm as the vacuum seal had been used by Alpert,[110] Brown and Coyle[111] and later workers,[112] and a design was developed from theirs which was capable of being constructed by rather less refined techniques than Brown and Coyle employed. Various materials were tested for reaction with benzil by heating a sample of benzil with a sample of the metal in a sealed pyrex tube at 200°C, for about fifteen hours. The melting point and ultra-violet spectrum were tests of the purity of the product. From the results of these tests, and also to reduce corrosion, nickel and stainless steel were chosen as materials for the valve.

A diagram of the valve is shown opposite. A big advantage of this design over a bellows-type valve is the small resistance to flow through the circulation line. The nickel seat had a concentric groove in its upper face to improve the tight fitting of the silver washer. When screwed down hard with the 6 inch key and open to the atmosphere, the valve allowed the 6-litre apparatus to leak overnight from high vacuum

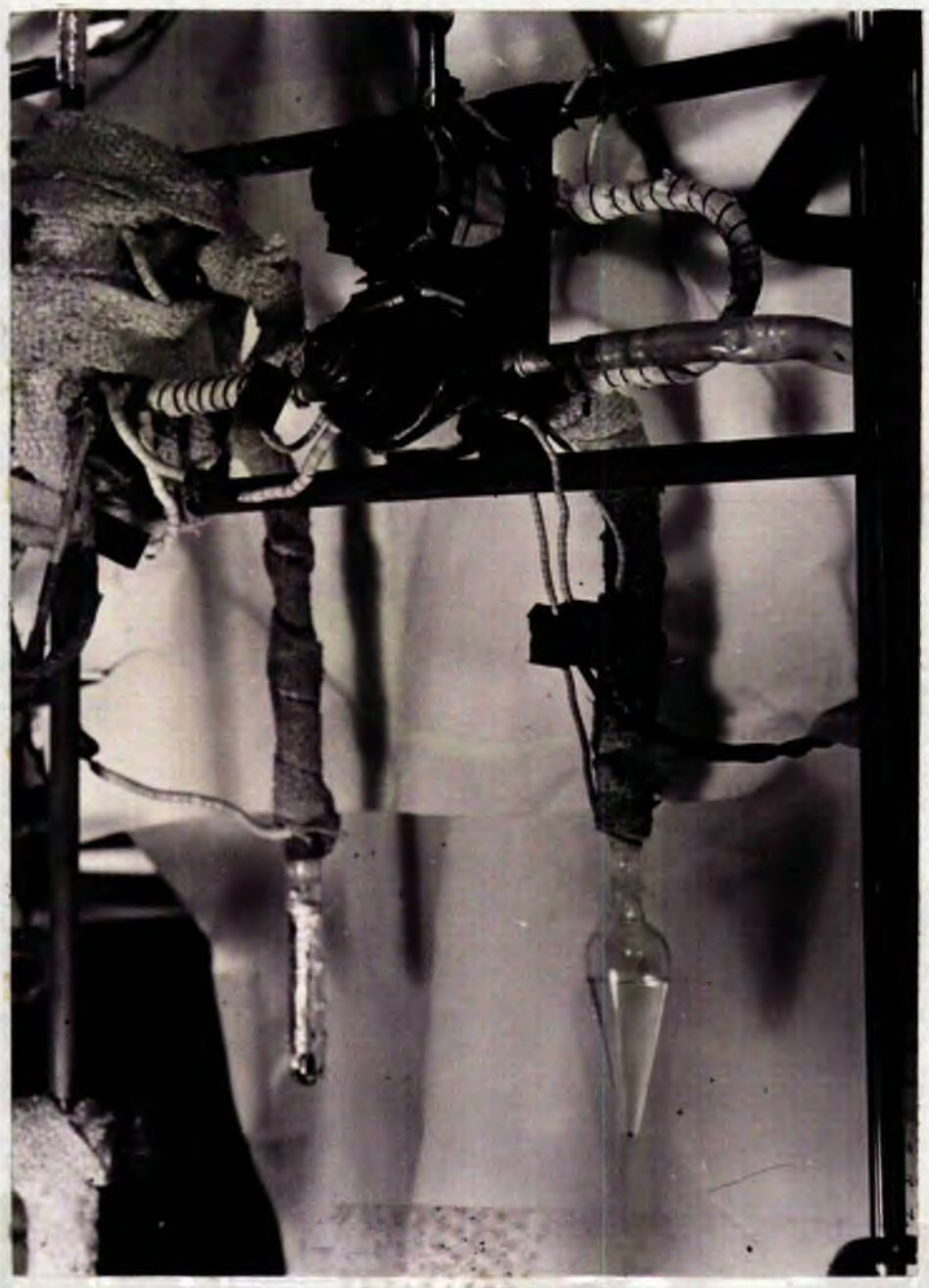


Fig.53.

to only 10^{-3} mm. mercury. During an experiment, the valve was only required to act as a "tap" for up to 50 mm. pressure of benzil, so this performance was quite adequate. Most of the valve was assembled and joined together with brass and hard silver solder. In use, the benzil container was attached by soft silver solder at DD'. Thus this joint at DD' could be softened, the tube removed, and the injection capillary changed, without affecting the other joints. The medium sized capillary was $\frac{1}{8}$ inch long, 0.018 inches diam. bore and was arranged to be directly under the valve seat, as shown. This elimination of dead space between capillary and valve prevented the build-up of benzil pressure behind the capillary and subsequent error in injection.

A valve similar to the one in the diagram, but without a capillary, was connected at CC' to act as an evacuation tap. Both valves were mounted in a steel frame and fitted with nichrome tape electrical heaters. The illustration opposite is of the toluene valve, which was identical in construction with the benzil valve.

Each time an experiment was started, the valve withdrawal nut was turned through the same angle (360°) so that the valve was opened a standard amount. The seat circumference was about 2 cm. and the throw of the valve thread 0.15 cm., so the open valve aperture was about 0.3 $cm.^2$.

After prolonged heating to 250°C and use, the nickel diaphragms fatigued, but could be replaced without too much difficulty.

APPENDIX 2

Calculation of standard Entropies.

As mentioned earlier, the methods can be divided into two groups:

(1) Summation of the translational and rotational etc. components for the standard entropy of molecules and radicals.

(2) Empirical methods of assessing thermodynamic properties based on the idea of group contributions.

(1) (a) Bensil.[113]

$$S^{\circ} = S^{\circ}tr. + S^{\circ}\,rot^{n} + \ldots.$$

The Sackur - Tetrode equation gives

$S^{\circ}tr. = 6.864 \log M + 25.99$ at $298^{\circ}K$, where M = MW.

Thus, for bensil,

$S^{\circ}tr. = 6.864 \log 210 + 25.99 =$ 41.7 eu.

The standard entropy contribution for rotation of the whole molecule is given by

$$S^{\circ}\,rot^{n} = 4.576\,(\tfrac{1}{2} \log IaIbIc + 3/2 \log T - \log \sigma + 58.51)$$

where σ = symmetry number,

Ia, Ib, Ic are the principal moments of inertia of the molecule.

For bensil, the moments of inertia were obtained by drawing a scale model of the molecule (bond lengths by comparison with dimensions of similar molecules)[109], and calculating $\sum m r^2$ about the three principal axes for all the atoms in the molecule.

The values obtained were: $I_a = 454 \times 10^{-40}$ gm.cm^2

$I_b = 3060 \times 10^{-40}$ " "

$I_c = 3480$ " "

Hence S° rot^n (benzil) $= 4.576 \left[\frac{1}{2} \log(3480 \times 3060 \times 454 \times 10^{-120}) + 5/2 \log 298 - \log 2 + 58.51 \right]$

$= \underline{35.0 \text{ eu}}$.

Calculation of the vibrational entropy contribution for other molecules suggests that at 298° K it is usually negligible.[88] Neglecting it and the contribution from internal rotation we obtain a value for benzil as a rigid rotator.

S° (benzil) $= \underline{75.2 \text{ eu}}$.

(b) The benzoyl radical.

From the Sackur-Tetrode equation

$S^\circ tr = 6.864 \log 105 + 25.99 = \underline{59.79 \text{ eu}}$.

The radical might be expected to have a very similar shape and mass to benzonitrile.[115] From microwave data, the principal moments of inertia of this molecule are available:

$I_a = 148.0 \times 10^{-40}$ gm cm^2

$I_b = 540$ " "

$I_c = 690$ " "

As a check, the PhCO- radical was drawn to scale, and its values of I_a and I_c were calculated as 124, and 685 x 10^{-40} gm.cm.^{2} respectively.

For benzonitrile and the benzoyl radical as rigid rotators.

$$S^{\circ}\ rot^{n} = 4.576\left[\tfrac{1}{2}\log\left(148 \times 540 \times 690 \times 10^{-120}\right) + 5/2\log 298 + 58.51\right]$$

$$= \underline{27.89\ eu.}$$

Thus

$$\triangle S^{\circ}(benzoyl)_{tr.+\ rot^{n}} = \underline{67.7\ eu.}$$

For PhCOCOPh = 2 PhCO-

$$S^{\circ} = 2(67.7) - 75.2$$

$$= \underline{60.2\ eu.}$$

(2) Jans[103] has reviewed several methods for the assessment of thermodynamic properties, and three of these were used.

(a) Anderson, Beyer and Watson's method.[95]

For this the entropy increments for the substition of methyl and other groups into the molecule substituent of greatest entropy can be assessed, and summation of all the increments when the compound has been built up, gives the total entropy.

For benzil, the summation can be tabulated:

Compound.	Entropy Increment for each substitution (eu)	Total Entropy (eu)
Ph H	64.4	64.4
Ph CH_3	12.0	76.4
Ph CH_2 CH_3	10.0	86.4
Ph CH_2 CH_2 CH_3	9.2	95.6
Ph CH_2 CH_2 Ph	21.7	117.3
Ph CHMe CHMe Ph	5.4	122.7
Ph CMe_2 CMe_2 Ph	2.8	125.5
Ph CO CO Ph	-4.8	120.5

Thus S^{o} (benzil) = 120.5 eu

S^{o} (dibenzyl) = 117.5 eu

(b) Souders, Matheus and Hurd's method.[116]

Increments have only been calculated for hydrocarbons, but the method gives a check on the entropy of dibenzyl.

For this method, increments are tabulated as entropies of formation. Thus, for dibenzyl:

Group	Entropy of formation.
2 $-CH_2-$	2(-25.37)
2 aliphatic $-\overset{\|\|}{C}-$	2(-9.49)
10 aromatic $-\overset{\|\|}{C}-H$	10(-5.43)

Total S^{o} (formation) = -120.12 eu.

Now, $S^{o}f = S^{o} - 1.36\,n - 15.615\,n$

where n = no. of carbon atoms

n = no. of hydrogen atoms.

S^{o} (dibenzyl) = -120.12 + 1.36(14) + 15.615(14)

= 116.38 eu.

There is a contribution for the symmetry number

= R ln σ = R ln 2 = 1.4 eu.

S^{o}(dibenzyl) = 118.38.

which is in reasonable agreement with the value from Anderson, Beyer and Watsons' method.

(c) "Group equations" method.[98]

A mathematical expression of the basis of this method is the

approximately held equation

$$S_{AB}^{\circ} = \tfrac{1}{2}(S_{A_2}^{\circ} + S_{B_2}^{\circ})$$

(i) $S^{\circ}_{PhCOCH_3} = 88.0$ (Calc[d] Anderson, Beyer and Watson)

$S^{\circ}_{C_2H_6} = 38.45$ [117]

$\therefore S^{\circ}$(benzil) = 2(88.0) - 38.45 = 117.5 eu.

(ii) $S^{\circ}_{PhCOC_2H_5} = 97.2$ (Calc[d] Anderson, Beyer and Watson)

S° n-butane = 73.5 [117]

S° (benzil) = 2(97.2) - 73.5 = 121.1 eu.

(iii) S°(PhCOPh) = 109.7 eu. (Calc[d] Anderson, Beyer and Watson)

S° PhPh = 98.1 eu. " " " "

$\therefore S^{\circ}$(benzil) = 2(109.7) - 98.1 = 121.3 eu.

All these values, however, depend on the accuracy of Anderson, Beyer and Watson's method.

For the estimation of S° (dibenzyl), more experimental entropy data is available.[117]

(iv) $S^{\circ}_{H_2} = 31.21$ eu.

$S^{\circ}_{PhCH_3} = 76.42$ eu.

$\therefore S^{\circ}$ (dibenzyl) = 121.63 eu.

(v) $S^{\circ}_{PhCH_2CH_3}$ = 86.15 eu.

$S^{\circ}_{C_2H_6}$ = 58.45 eu.

$\therefore$ S° (dibenzyl) = 117.2 eu. Average = 120 eu.

The entropy of the benzyl radical is probably very close to that of toluene i.e. 76.42 eu.

$\therefore$ For the process $PhCH_2CH_2Ph$ = $2PhCH_2$-

ΔS° = 2(76.42) - 120

= 32.8 eu.

If the standard entropy of bensil were 120 eu, ΔS° for the dissociation of bensil would be only

= 2(67.7)- 120 = 15.4 eu.

which seems much too small in view of the previous discussion, and the similarity of the processes in the dissociations of bensil and dibenzyl. The methods of estimation of entropy by group contribution do not allow for such as conjugation effects, and bensil almost certainly has some conjugation of the Ph and CO groups. This would mean that S° bensil is less than 120 eu, and earlier comparisons suggest ~ 30 - 40 eu. A more reliable estimate by the group contribution methods would be possible if experimental entropy data were available for compounds containing the benzoyl group.

TABLE OF EXPERIMENTAL RESULTS

Unless otherwise stated, the carrier gas was Argon, at a pressure of about 2.2 mm.

(a) Preliminary Experiments with benzil alone.

Expt.	Temperature (°C)	Contact time (secs)	P_{benzil} (mm)	Percentage Decomposition
1	524	0.67	0.13	0.196
2	527	0.68	0.15	0.315
3	528	0.67	0.15	0.307
4	528	0.66	0.125	0.355
5	525	0.72	0.102	0.102
6	527	0.72	0.105	0.105
7	528	0.73	0.107	0.107
8	529	0.74	0.108	0.108
9	529	0.745	0.110	0.110
10	532	0.67	0.16	0.306
11	532	0.65	0.15	0.335
12	528	0.69	0.16	0.375
13	528	0.71	0.17	0.425
14	527	0.62	0.17	0.355
15	528	0.74	0.17	0.392
16	529	0.65	0.18	0.48
17	529	0.65	0.18	0.61

(b) Experiments with benzil and toluene.

Expt.	Temperature (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	percentage decomposition
(1)	Variation of toluene partial pressure				
18	525	0.71	0.116	0.75	0.07
19	526	0.72	0.111	0.76	0.15
20	526	0.715	0.115	0.76	0.09
21	526	0.94	0.145	0.98	0.105
22	527	0.95	0.15	0.99	0.106
23	563	0.65	0.112	0	1.30
24	563	0.67	0.103	0.65	0.78
25	563	0.66	0.131	0	2.20
26	564	0.66	0.121	0	2.55
27	564	0.54	0.100	0.60	0.82
28	564	0.55	0.100	0.60	1.25
29	557	0.65	0.06	0.95	2.10
30	557	0.65	0.045	0.72	1.95
31	557	0.71	0.05	0.37	2.05
32	557	0.72	0.04	0	3.90
33	549	0.90	0.11	0	4.62
34	540	0.90	0.102	0.126	5.82
35	549	0.90	0.09	0.475	8.95

Expt.	Temperature (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	percentage decomposition
(2) Variation of benzil partial pressure.					
36	540	0.56	0.035	1.02	1.11
37	540	0.57	0.056	1.08	1.45
38	540	0.55	0.060	0.96	1.81
39	540	0.55	0.134	2.15	2.01
40	540	0.55	0.218	2.50	2.52
41	540	0.55	0.276	1.79	2.37
42	540	0.56	0.275	1.97	1.88
43	540	0.55	0.31	2.27	2.21
44	540	0.56	0.396	1.91	1.99
45	540	0.55	0.415	1.92	2.38
46	540	0.55	0.46	1.91	2.37
(3) Variation of contact time.					
47	559	0.535	0.125	1.90	0.95
48	559	1.22	0.130	2.16	2.18
49	559	1.54	0.109	2.14	2.77
50	559	2.68	0.05	2.02	4.63
51	597	0.40	0.27	1.19	15.0
52	597	0.45	0.30	1.19	16.4
53	597	0.395	0.215	1.12	22.5
54	597	0.395	0.48	1.11	18.8

Expt.	Temperature (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	percentage decomposition
55	597	0.72	0.16	0.75	25.5
56	597	0.75	0.14	0.74	25.5
57	597	0.85	0.125	0.84	24.0
58	597	1.07	0.214	0.96	29.4
59	597	1.18	0.255	0.815	27.2
60	597	1.24	0.19	0.76	27.5
61	597	1.62	0.20	0.80	34.1
62	597	1.69	0.21	0.82	35.8
63	597	2.23	0.14	1.17	37.9
64	597	2.52	0.15	1.11	37.9

(4) <u>The effect of carbon monoxide as a carrier gas</u>.

Carrier gas pressure = 2 mm.

Expt.	Temp. (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	Carrier gas	percentage decomposition
65	598	0.70	0.197	1.08	Ar	19.5
66	598	0.70	0.151	1.56	CO	25.8
67	598	0.70	0.41	1.49	Ar	19.9
68	598	0.70	0.30	1.41	CO	19.2

(5) Measurement of carbon produced.

Expt.	Temperature (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	moles carbon deposited.
83	666	0.51	0.156	1.55	5.20×10^{-4}
84	665	0.52	0.146	1.50	5.20×10^{-4}
85	660	0.49	0.145	1.54	6.40×10^{-5}
86	658	0.95	0.145	0.79	1.14×10^{-4}

(6) Measurement of methane and hydrogen produced.

Expt.	Temp. (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	moles hydrogen	moles methane
87	659	0.52	0.056	1.59	1.05×10^{-4}	1.0×10^{-5}
88	654	0.55	0.076	1.60	1.55×10^{-4}	1.50×10^{-5}

(7) Determination of temperature coefficient for benzil rate equation

Expt.	Temperature (°C)	Contact time (secs)	percentage decomposition	$\log_{10}k_{uni}+3$	$10^3/T(°K)$
69	666	0.497	65.7	3.352	1.065
70	666	0.490	61.0	3.295	1.065
71	641	0.525	55.6	3.167	1.094
72	659	0.53	50.9	3.128	1.096
73	625	0.485	38.6	3.005	1.116
74	624	0.56	38.4	2.942	1.114

Expt.	Temperature (°C)	Contact time (secs)	percentage decomposition	$\log_{10} k_{uni}$ +5	$10^5/T(°K)$
75	596	0.55	20.2	2.614	1.151
76	597	0.56	25.0	2.667	1.149
77	570	0.68	11.7	2.261	1.174
78	579	0.58	12.0	2.365	1.174
79	579	0.57	10.6	2.292	1.174
80	558	0.55	4.85	1.956	1.205
81	558	0.56	4.76	1.939	1.205
82	559	0.55	3.82	1.848	1.205
90	539	0.55	1.81	1.519	1.232
91	520	0.52	0.748	1.156	1.261
92	511	0.58	0.419	0.897	1.276
95	494	0.61	0.196	0.508	1.304
94	488	0.61	0.144	0.368	1.314
95	482	0.54	0.139	0.417	1.325
96	482	0.59	0.095	0.308	1.325
97	468	0.62	0.078	0.101	1.350
98	466	0.56	0.068	0.020	1.353

(8) Heterogeneity tests

Expt.	Temperature (°C)	Contact time (secs)	S/V ratio	$\log_{10} k_{uni} + 5$	$10^3/T$ (°K)
99	476	0.30	6.66	0.060	1.355
100	505	0.31	6.66	0.301	1.329
101	527	0.493	6.66	1.136	1.250
102	527	0.493	6.66	1.100	1.250
103	476	0.65	1.59	0.995	1.328
104	500	0.65	1.59	0.500	1.304
105	522	0.650	1.59	1.306	1.347
106	525	0.505	1.59	1.531	1.346

(9) Reaction in a static system.

(a) Low conversion.

Expt.	Temp. (°C)	Contact time (secs)	P_{benzil} (mm)	$P_{toluene}$ (mm)	$\log_{10} k_{uni} + 7$	$10^3/T$(°K)
107	404	215	55.5	300	1.512	1.477
108	502	120	54.5	402	0.955	1.337
109	502	300	55.5	402	0.118	1.373

(b) High conversion for qualitative analysis.

Expt.	Temperature (°C)	Contact time (secs)	p_{benzil} (mm)	$p_{toluene}$ (mm)	percentage decomposition
110	460	180	141.0	555	38.9
111	460	180	15.2	579	65.9
112	460	180	7.8	508	79.8
113	460	180	5.06	417	85.9
114	460	180	72.0	492	85.1
115	460	180	35.8	476	87.0
116	460	180	5.15	397	78.2
117	460	180	5.15	406	67.7

Thermal decomposition of deoxybenzoin in excess toluene.

Expt.	Temperature (°C)	Contact time (secs)	$p_{deoxybenzoin}$ (mm)	$p_{toluene}$ (mm)	percentage decomposition
(1) Variation of toluene partial pressure.					
118	601	0.40	0.137	0	4.18
119	601	0.40	0.318	0.376	4.10
120	601	0.40	0.127	0.306	4.32
121	601	0.40	0.144	0.690	4.10

Expt.	Temperature (°C)	Contact time (secs)	$p_{desoxybenzoin}$ (mm)	$p_{toluene}$ (mm)	percentage decomposition
(2) Variation of desoxybenzoin partial pressure.					
122	631	0.595	0.27	1.14	4.99
123	631	0.572	0.0675	1.22	4.59
124	631	0.550	0.050	1.34	4.06
125	631	0.558	0.015	1.41	4.25
(3) Variation of contact time.					
126	629	0.538	0.137	1.11	1.77
127	629	1.01	0.077	1.04	3.05
128	629	1.00	0.51	1.09	3.10
129	629	2.00	0.135	1.56	15.10
130	629	2.10	0.507	0.92	18.50

(4) Determination of temperature coefficient for desoxybenzoin rate equation.

Expt.	Temperature (°C)	Contact time (secs)	percentage decomposition	$\log_{10}k_{uni}+3$	$10^3/T$ (°K)
131	615	0.535	6.00	2.255	1.135
132	614	0.402	6.90	2.221	1.137
133	571	0.555	2.19	1.930	1.155
134	571	0.577	1.96	1.881	1.155
135	550	0.507	1.04	1.573	1.208
136	550	0.575	0.915	1.504	1.208

Expt.	Temperature (°C)	Contact time (secs)	percentage decomposition	$\log_{10} k_{uni} + 3$	$10^3/T$ (°K)
137	555	0.590	1.00	1.255	1.308
138	535	0.575	0.329	0.761	1.241
139	521	0.72	0.37	0.712	1.359
140	516	0.595	0.302	0.534	1.267
141	513	0.603	0.141	0.367	1.272

(5) Heterogeneity Test.

Expt.	Temperature (°C)	Contact time (secs)	S/V ratio	$\log_{10} k_{uni} + 3$	$10^3/T$ (°K)
142	500	0.61	6.66	0.008	1.294
143	511	0.618	6.66	0.180	1.276
144	521	0.638	6.66	0.364	1.259
145	529	0.645	6.66	0.630	1.247
146	509	0.675	1.99	0.249	1.279
147	521	0.685	1.99	0.500	1.259
148	529	0.71	1.99	0.660	1.247

(6) Reaction under static conditions.

Expt.	Temp. (°C)	Contact time (secs)	P_{dec} (mm)	$P_{toluene}$ (mm)	$\log_{10} k_{uni} + 6$	$10^3/T$ (°K)
149	451	250	57.0	552	0.255	1.429

Reactions with excess hydrogen iodide.

(a) Benzil. For these experiments P_{benzil} was about 0.05 mm.

Expt.	Temp. (°C)	Contact time (secs)	gm. atoms iodine	moles carbon monoxide	$\log_{10}k_{uni}+4$	$10^3/T(°K)$
150	586	0.54	2.58×10^{-4}	5.27×10^{-5}	3.440	1.164
151	529	0.64	1.65×10^{-4}	4.64×10^{-6}	2.241	1.247
152	547	0.77	4.25×10^{-4}	9.75×10^{-6}	2.755	1.217
153	475	0.81	1.51×10^{-4}	2.16×10^{-6}	0.965	1.357
154	403	0.91	-	-	-	
155	585	0.317	4.25×10^{-4}	7.10×10^{-5}	3.549	1.164
156	585	0.76	2.64×10^{-4}	5.27×10^{-5}	3.253	1.164

Expt.	Temperature (°C)	P_{benzil} (mm)	P_{HI} (mm)	moles iodine produced
159	500	0.059	0.17	2.80×10^{-5}
160	500	0.04	0.27	1.75×10^{-5}
161	500	0.055	0.46	3.50×10^{-5}
162	500	0.05	0.79	4.47×10^{-5}
163	500	0.042	0.76	1.78×10^{-4}

(b) Benzaldehyde.

Expt.	Temp. (°C)	Contact time (secs)	$P_{benzaldehyde}$ (mm)	P_{HI} (mm)	gm. atoms iodine	percentage decomposition to carbon monoxide.
157	549	0.60	0.25	0.56	5.2×10^{-5}	0.19
158	547	0.89	0.24	0.66	7.8×10^{-6}	0.20

(c) Benzylbenzoin. ($P_{deoxybenzoin}$ = 0.15 mm.)

Expt.	Temp. (°C)	Contact time (secs)	gm.atoms iodine	moles carbon monoxide	$\log_{10} k'_{uni} + 5$	$10^5/T(°K)$
164	511	0.76	-	1.36×10^{-6}	0.118	1.376
165	564	0.59	7.0×10^{-6}	9.30×10^{-6}	1.089	1.187

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